

Linear Optical and Third-Order Nonlinear Optical Properties of Some Fluorenyl- and Triarylamine-Containing Tetra-cyanobutadiene Derivatives

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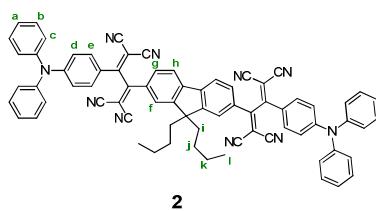
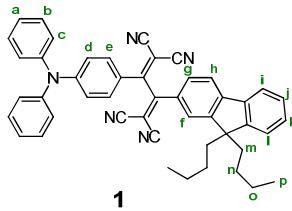
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1. Synthesis of 2,7-diodo-9,9-dibutylfluorene (9)

A solution of KOH (23.856 g, 0.426 mol, 10 eq.) and tetrabutylammonium bromide (2.748 g, 0.0426 mol, 6 eq.) in water (35 mL) was heated to 65 °C. After a few minutes, 2,7-diodofluorene (17.8g, 0.426 mol, 1 eq.) and bromobutane (35.02 g, 0.256 mol, 6 eq.) were added and the mixture turned deep red. After 1 h heating, the mixture was cooled to 20 °C and a suspension formed in the biphasic reaction medium. The pink aqueous phase and violet organic phase were separated from the solid. The aqueous phase was extracted with CH₂Cl₂ (3 x 100 mL) and the dark brown extracts were combined with the organic phase and dried over MgSO₄ before being evaporated. After three recrystallizations from EtOH, the pure title compound was isolated as an orange solid (17.90 g, 79%) and characterized by comparison to literature.¹ **MP:** 130-131 °C. **R_f:** 0.71 [hexane] **¹H-NMR** (400 MHz, CDCl₃): δ = 7.61-7.69 (m, 4H, H_{Ar}), 7.41 (d, ³J_{H,H} = 7.4 Hz, 2H, H_{Ar}), 1.86-1.93 (m, 4H, H_{Bu}), 1.02-1.16 (m, 4H, H_{Bu}), 0.69 (t, ³J_{H,H} = 7.3 Hz, 6H, H_{Bu}), 0.56 (m, 4H, H_{Bu}). **¹³C{¹H}-NMR** (101 MHz, CDCl₃): δ = 153.0, 140.3, 136.6, 132.5, 122.1, 94.0, 56.0, 40.5, 26.4, 23.5, 14.5.

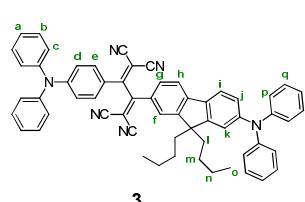
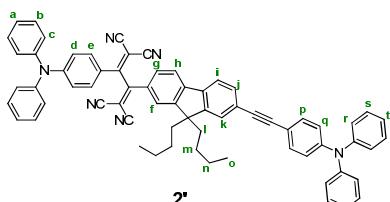
¹ D. Li, H. Li, M. Liu, J. Chen, J. Ding, X. Huang and H. Wu, *Macromol. Chem. Phys.*, 2014, **215**, 82-89.

2. ^1H / $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of 1-4 and Assignment of Signals



Compound 1: ^1H NMR (400 MHz, CDCl_3) δ = 7.83 (1H, d, J 1.5 Hz, H_f), 7.72 (1H, d, J 8.1 Hz, H_h), 7.71-7.67 (1H, m, H_i), 7.61 (2H, d, J 9.3 Hz, H_d), 7.46 (1H, dd, J 1.9 and 8.1 Hz, H_g), 7.39-7.28 (7H, m, H_b , H_j , H_k and H_l), 7.21-7.11 (6H, m, H_a and H_c), 6.86 (2H, d, J 9.3 Hz, H_e), 2.03-1.85 (4H, m, H_m), 1.05-0.92 (4H, m, H_o), 0.57 (6H, t, J 7.3 Hz, H_p), 0.54-0.44 (4H, m, H_n). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ = 168.9, 164.7, 153.8, 152.6, 152.3, 148.2, 144.7, 139.0, 132.1, 130.3, 130.2, 129.9, 129.4, 127.6, 127.1, 126.8, 124.5, 123.4, 122.0, 121.4, 121.0, 118.2, 113.8, 112.8, 112.8, 111.9, 85.1, 78.6, 55.8, 39.9, 26.1, 23.0, 13.9.

Compound 2: ^1H NMR (400 MHz, CDCl_3): δ = 7.93 (2H, d, J 1.7 Hz, H_f), 7.89 (2H, d, J 8.1 Hz, H_h), 7.70 (4H, d, J 9.3 Hz, H_d), 7.57 (2H, dd, J 1.7 and 8.1 Hz, H_g), 7.45-7.37 (8H, m, H_b), 7.32-7.20 (12H, m, H_a and H_c), 6.96 (4H, d, J 9.3 Hz, H_e), 2.15-2.00 (4H, m, H_i), 1.13-1.00 (4H, m, H_k), 0.64 (6H, t, J 7.3 Hz, H_f), 0.61-0.50 (4H, m, H_j). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 168.3, 163.6, 153.8, 153.4, 144.8, 144.3, 132.2, 131.9, 130.0, 129.2, 126.9, 126.8, 124.6, 122.3, 121.3, 117.9, 113.6, 112.8, 112.2, 111.4, 87.0, 78.0, 56.4, 39.3, 25.9, 22.7, 13.7.



Compound 2': ^1H NMR (400 MHz, CDCl_3): δ = 7.83 (1H, d, J 1.6 Hz, H_f), 7.70-7.71 (1H, d, J 8.1 Hz, H_h), 7.64 (1H, dd, J 0.8 and 7.7 Hz, H_i), 7.61 (2H, d, J 9.3 Hz, H_d), 7.48-7.46 (1H, m, H_g), 7.44 (2H, br s, H_i and H_k), 7.36-7.28 (6H, m, H_b and H_q), 7.24-7.11 (10H, m, H_a , H_r and H_s), 7.07-7.03 (4H, m, H_c), 7.00 (2H, tt, J 1.1 and 7.3 Hz, H_i), 6.94 (2H, d, J 8.8 Hz, H_p), 6.86 (2H, d, J 9.3 Hz, H_e), 2.03-1.85 (4H, m, H_i), 1.05-0.94 (4H, m, H_n), 0.58 (6H, t, J 7.3 Hz, H_o), 0.55-0.39 (4H, m, H_m). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 168.6, 164.5, 153.8, 152.6, 152.5, 148.3, 147.3, 147.2, 144.6, 138.6, 132.7, 132.0, 131.1, 130.5, 130.2, 129.5, 129.4, 127.0, 126.8, 126.1, 125.2, 124.9, 124.4, 123.8, 122.1, 122.0, 121.3, 121.1, 118.1, 115.6, 113.7, 112.8, 112.7, 111.9, 91.9, 89.4, 85.2, 78.5, 55.8, 39.8, 26.0, 23.0, 13.9.

Compound 3: ^1H NMR (400 MHz, CDCl_3): δ = 7.92 (1H, d, J 1.5 Hz, H_f), 7.75 (2H, d, J 9.2 Hz, H_d), 7.71 (1H, d, J 8.2 Hz, H_h), 7.65-7.57 (2H, m, H_g and H_i), 7.43 (4H, t, J 7.8 Hz, H_p), 7.37-7.24 (10H, m, H_c , H_q and H_t), 7.20 (4H, d, J 7.6 Hz, H_b), 7.14 (3H, m, H_a and H_k), 7.12-7.05 (1H, m, H_j), 7.00 (2H, d, J 9.2 Hz, H_e), 2.07-1.83 (4H, m, H_i), 1.19-1.06 (4H, m, H_n), 0.75 (6H, t, J 7.3 Hz, H_o), 0.72-0.63 (4H, m, H_m). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ = 168.3, 165.0, 154.3, 153.7, 151.9, 150.0, 148.3, 147.4, 144.6, 132.9, 132.0, 130.2, 129.8, 129.5, 129.1, 127.0, 126.7, 125.0, 124.1, 123.8, 122.2, 122.1, 120.0, 118.1, 117.2, 113.8, 113.1, 112.8, 112.2, 83.4, 78.6, 55.5, 39.6, 26.1, 22.9, 13.9.

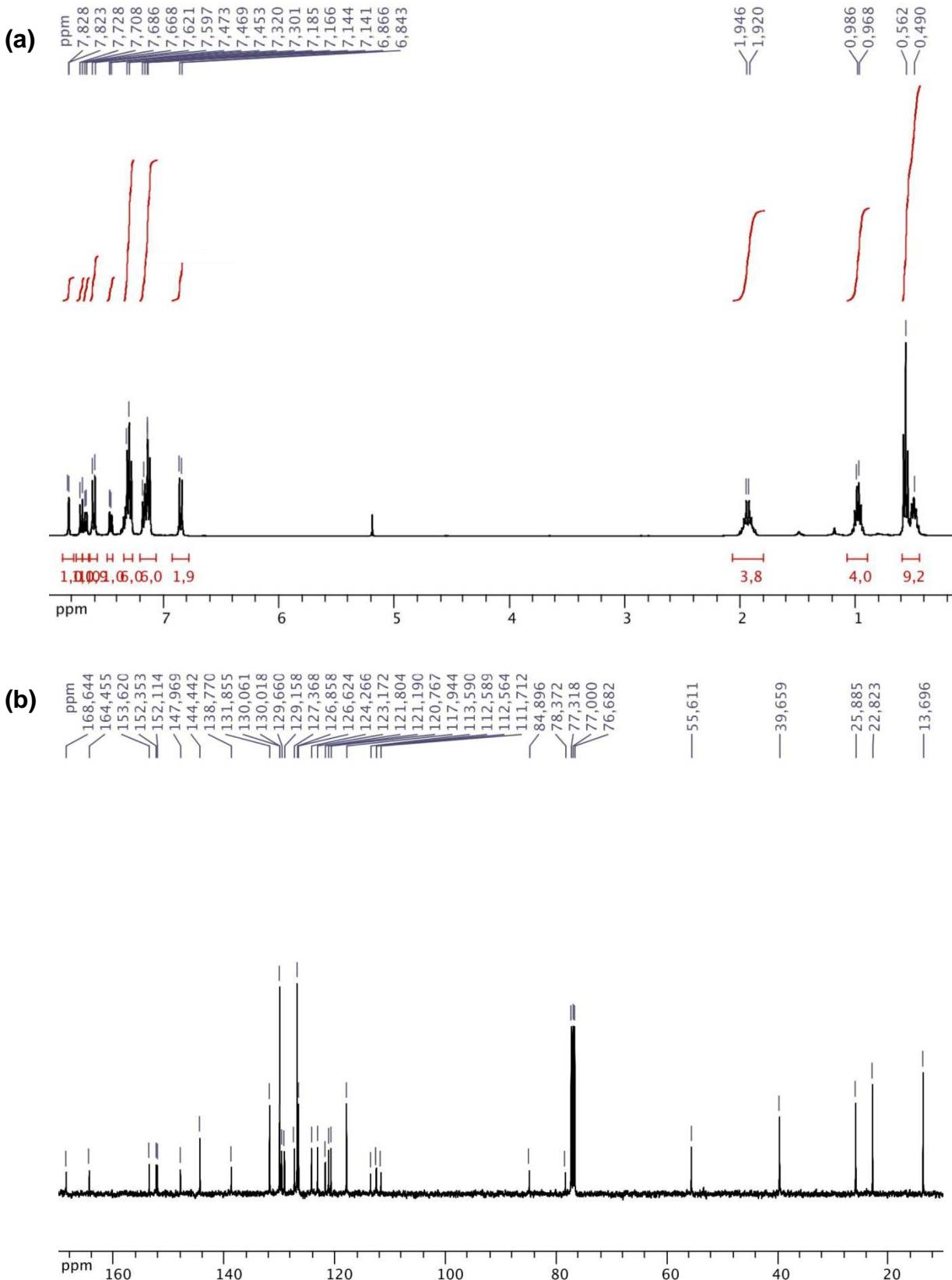
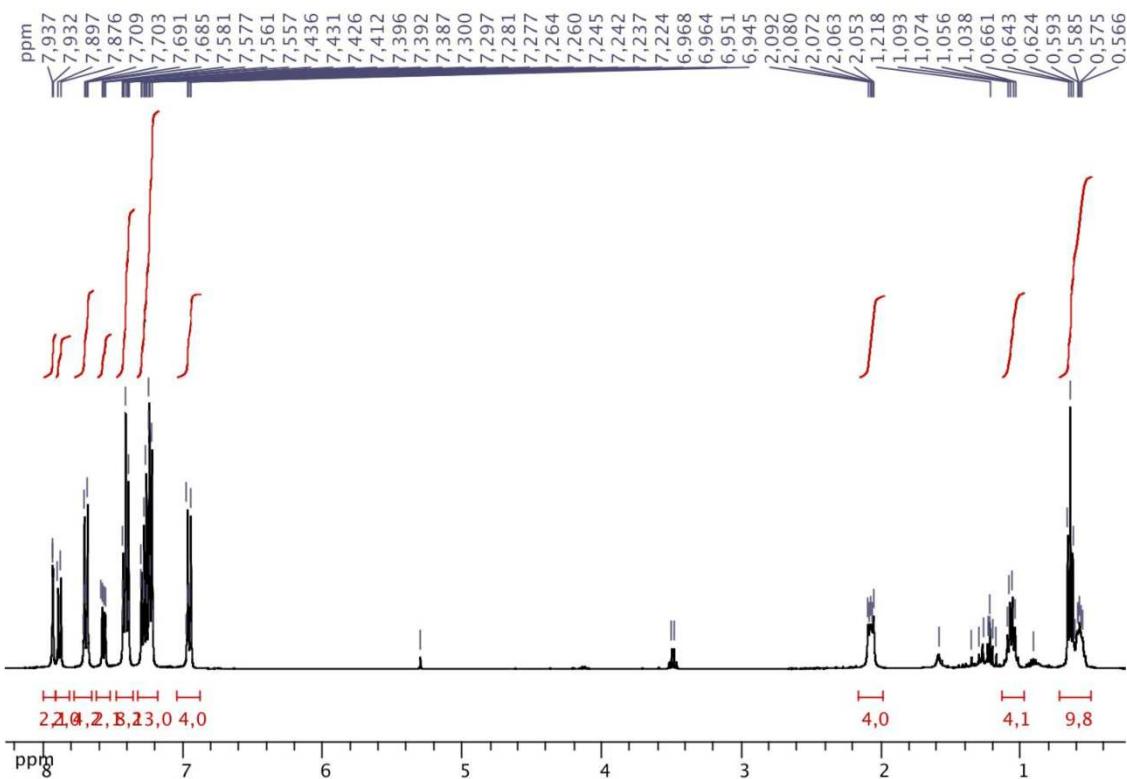


Figure S1. ^1H (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR Spectra at 400 and 100 MHz, respectively, for **1** in CDCl_3 .

Supporting Information

(a)



(b)

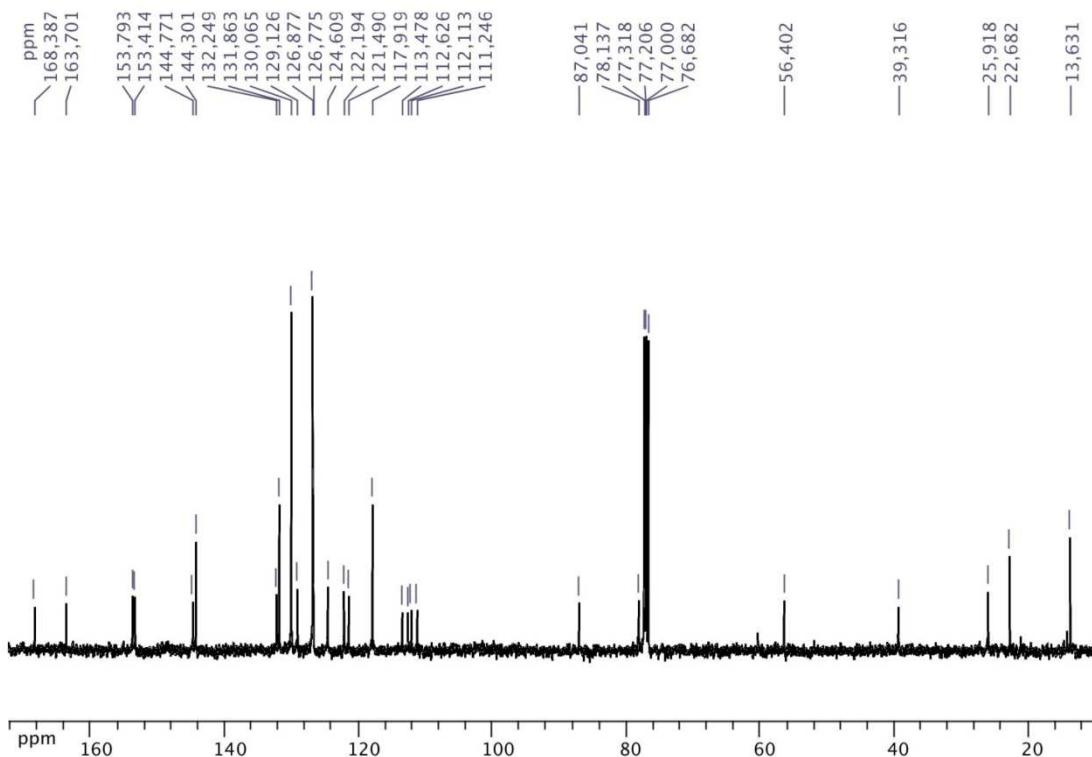


Figure S2. ^1H (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR Spectra at 400 and 100 MHz, respectively, for **2** in CDCl_3 .

Supporting Information

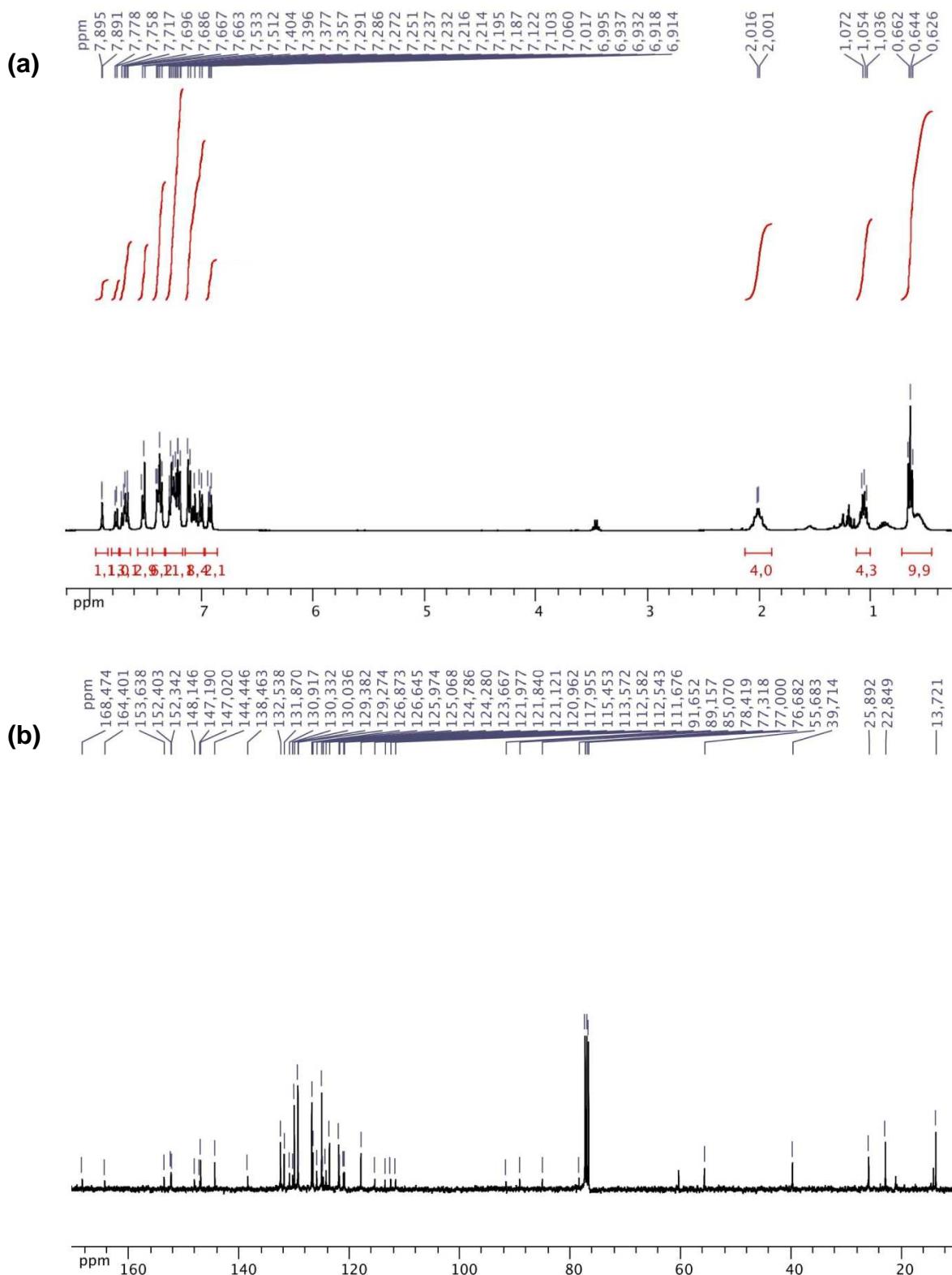


Figure S3. ^1H (a) and $^{13}\text{C}\{\text{H}\}$ (b) NMR Spectra at 400 and 100 MHz, respectively, for **2'** in CDCl_3 .

Supporting Information

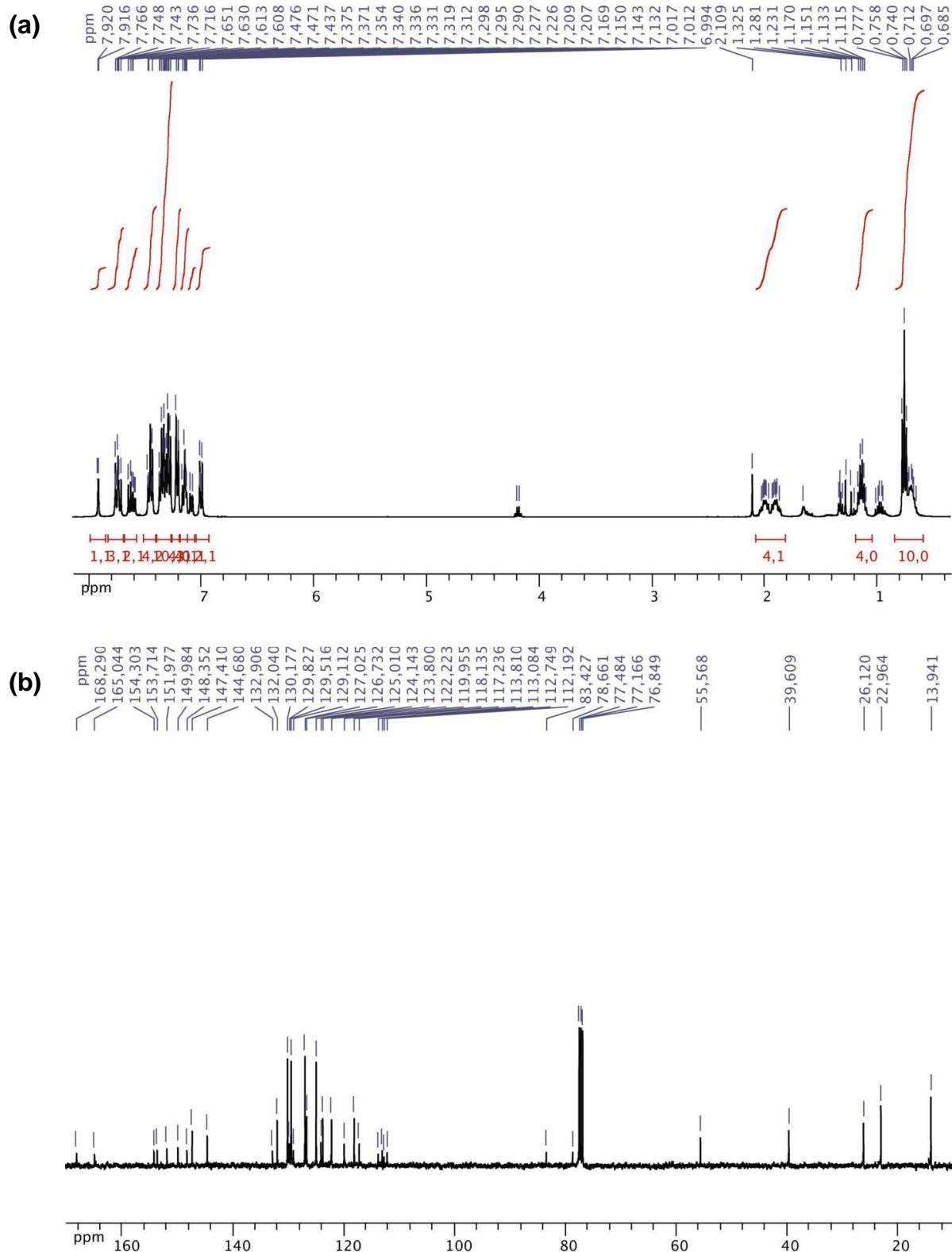


Figure S4. ^1H (a) and $^{13}\text{C}\{^1\text{H}\}$ (b) NMR Spectra at 400 and 100 MHz, respectively, for **3** in CDCl_3 .

3. Characteristic Vibrational Modes Detected by IR/Raman Spectroscopy for 1-6

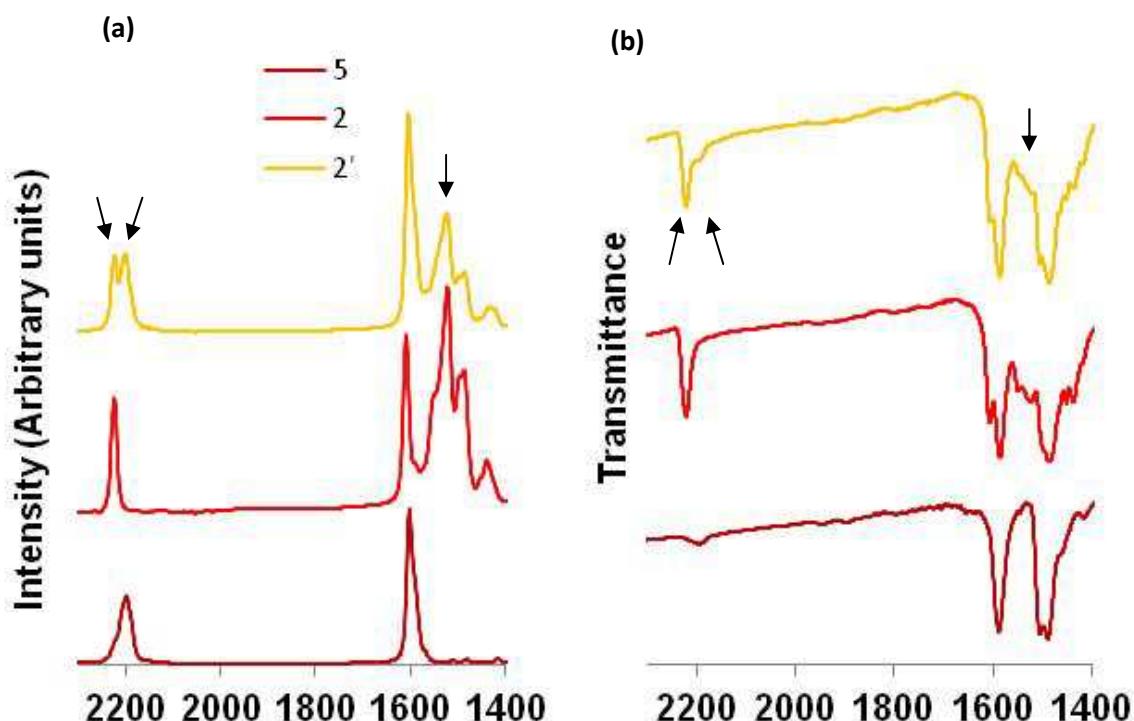


Figure S5. Comparison between Raman (a) and IR (b) spectra of **5**, **2** and **2'** in the 2300-1900 cm⁻¹ spectral region showing the $\nu_{C=C}/\nu_{C=N}$ modes. The presence of one of each in **2'** is clearly evidenced by Raman. Additional modes near 1550 cm⁻¹ which might be attributed to $\nu_{C=C}$ modes of TCBD are also apparent in **2** and **2'**.

4. UV-Vis Absorption Solvatochromy for 1-3

Table S1. Absorption Solvatochromy for **1-3** and **2'**.

| Solvent | 1 | 2 | 2' | 3 |
|--------------------------|--|--|--|--|
| | $\lambda_{\text{abs}}^{\text{max } 1}$ (nm) | $\lambda_{\text{abs}}^{\text{max } 2}$ (nm) | $\lambda_{\text{abs}}^{\text{max } 1}$ (nm) | $\lambda_{\text{abs}}^{\text{max } 1}$ (nm) |
| Toluene | 412 | 487 | 429 | 406 |
| AcOEt | 401 | 472 | 413 | 392 |
| SOAG | 405 | 479 | 418 | 396 |
| THF | 405 | 478 | 420 | 396 |
| CH_2Cl_2 | 415 | 487 | 428 | 411 |
| EtOH | 406 | 479 | 419 | 398 |

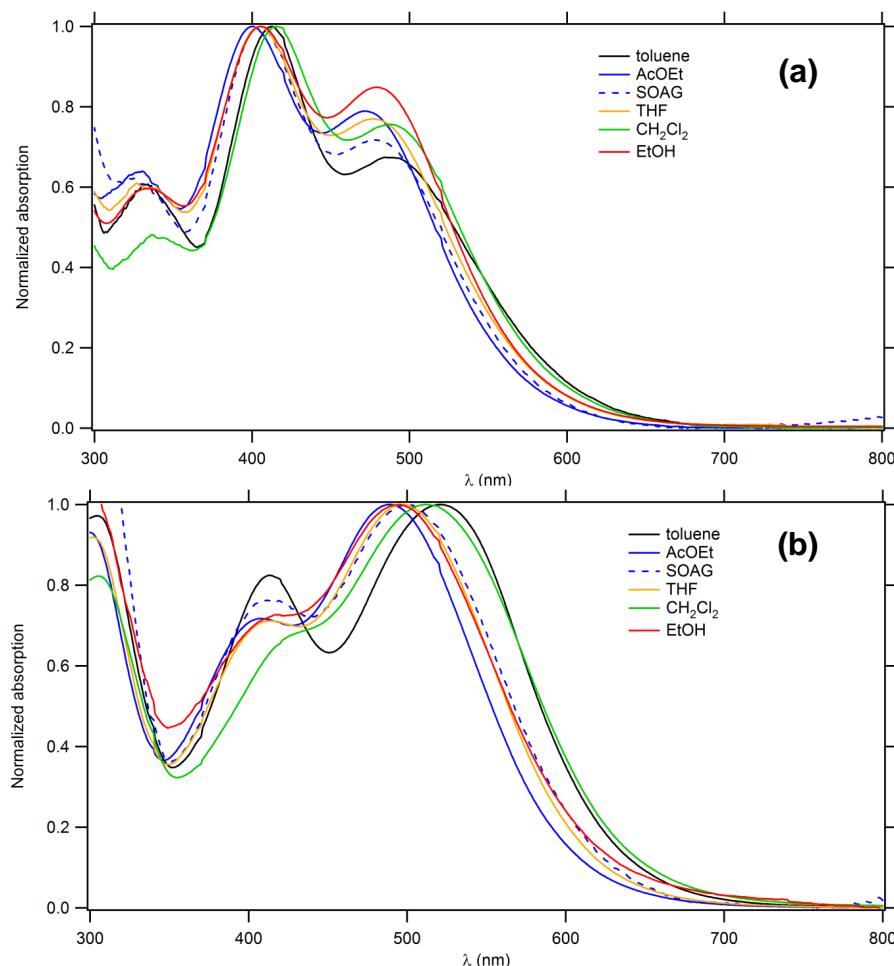


Figure S6. UV-Vis spectra of **1** (a) and **3** (b) in various solvents at 25 °C.

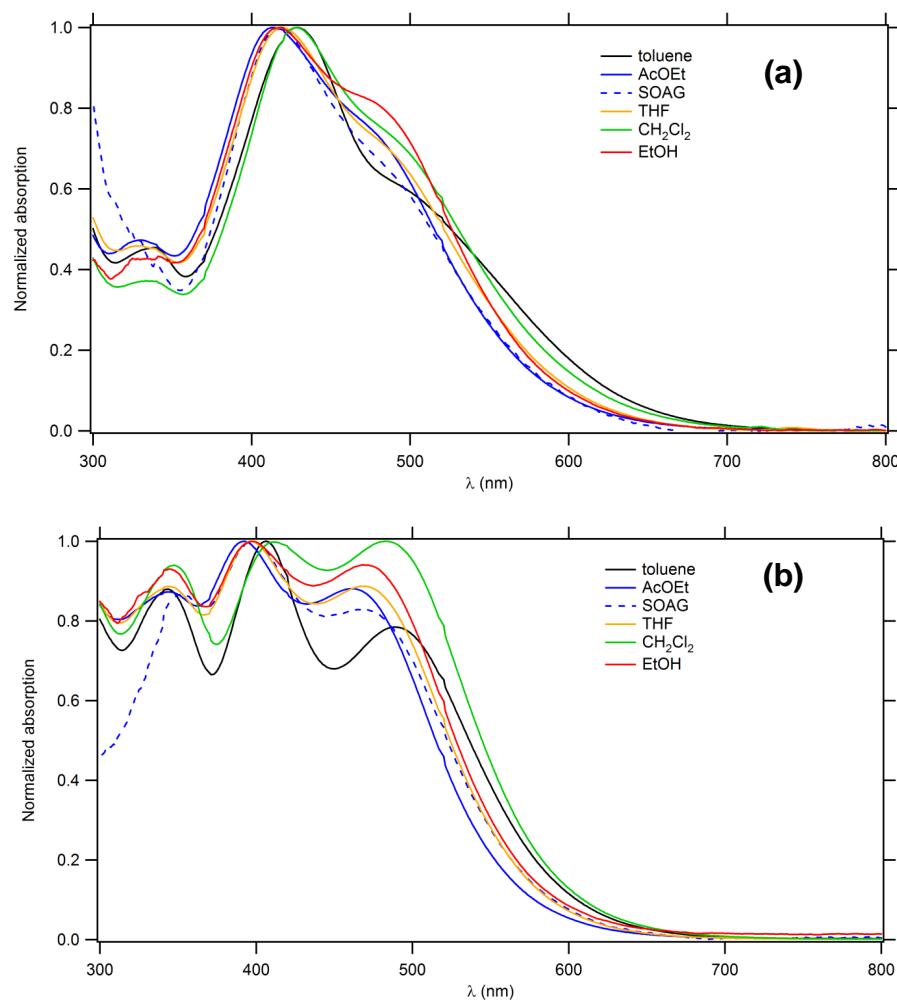


Figure S7. UV-Vis spectra of **2** (a) and **2'** (b) in various solvents at 25 °C.

5. UV-Vis Absorption and Emission Spectra for 1-3 in Solvent Glasses

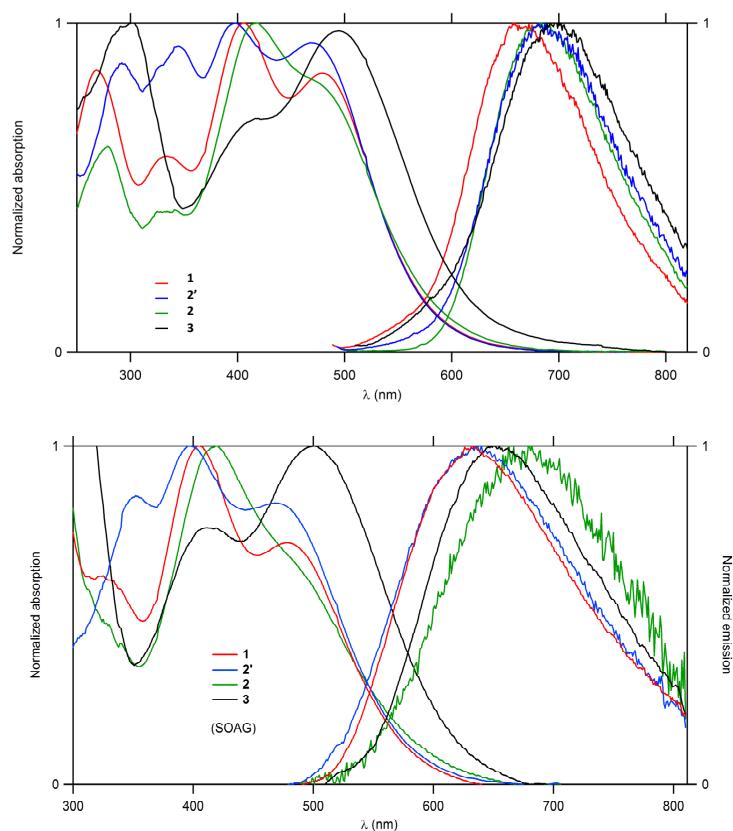


Figure S8. Mirror images of the absorption spectra at 298 K and of the normalized emission spectra for **1**, **2**, **2'** and **3** in (a) ethanol at 77 K and (b) in sucrose octaacetate at 298 K.

Table S2. Absorption and Emission Data for **1-3** in solvent glasses

| Cmpd | Absorption λ (nm) | Stokes Shift (cm ⁻¹) | Emission ^[a] λ _{em} (nm) [Φ _{em}] | λ _{0,0} (nm / eV) |
|--------------|----------------------|-------------------------------------|--|-------------------------------|
| EtOH at 77 K | | | | |
| 1 | 334, 406, 479 | 5817 | 664 [0.12] | 574 / 2.16 ^[b] |
| 2' | 2345, 398, 469 | 6702 | 684 [0.11] | 586 / 2.12 ^[b] |
| 2 | 337, 419, 474 (sh) | 6434 | 682 [0.08] | 596 / 2.08 ^[b] |
| 3 | 419, 495 | 5834 | 696 [0.06] | 600 / 2.07 ^[b] |
| SOA at 298 K | | | | |
| 1 | 325, 405, 479 | 5054 | 632 [0.06] | 547 / 2.27 |
| 2' | 352, 396, 468 | 5619 | 635 [0.05] | 545 / 2.28 |
| 2 | 420, 486 (sh) | 5783 | 676 [0.02] | 564 / 2.20 |
| 3 | 412, 501 | 4623 | 652 [0.06] | 579 / 2.14 |

[a] Fluorescence quantum yield determined relative to rhodamine 101 in EtOH at the same temperature ($\Phi_F = 1$).² [b] Obtained from absorption and emission spectra determined at different temperatures.

² A. M. Brouwer, *Pure Appl. Chem.* **1980**, *83*, 2213-2228.

6. UV-Vis Absorption and Emission Spectra for 4-6 and Solvatochromy

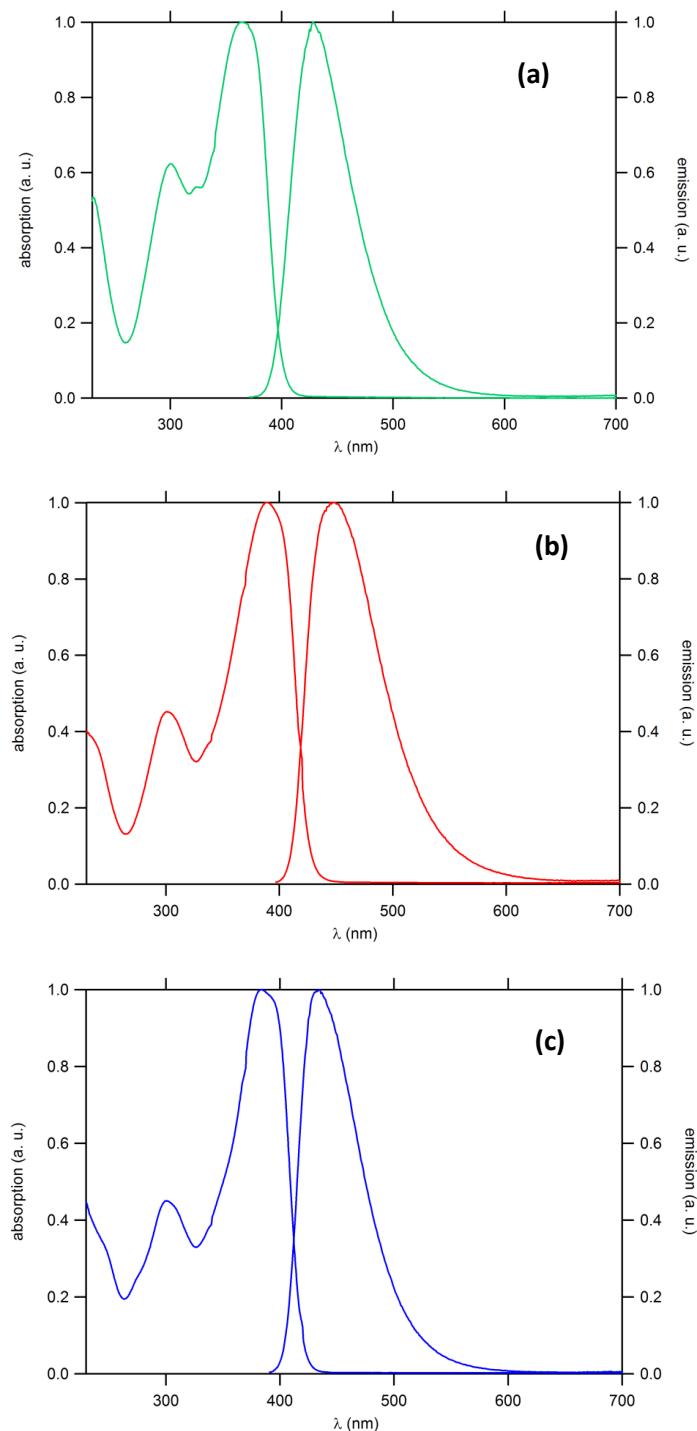


Figure S9. Mirror images of the absorption and rescaled emission spectra for **4** (a), **5** (b) and **6** (c) in dichloromethane (20 °C).

Table S3. Absorption Solvatochromy for **1-3** and **2'**.

| Solvant | 4 | 5 | 6 | | | |
|--------------------------|---|--|---|--|---|--|
| | $\lambda_{\text{abs}}^{\text{max}}$ (nm) | $\lambda_{\text{em}}^{\text{max}}$ (nm) | $\lambda_{\text{abs}}^{\text{max}}$ (nm) | $\lambda_{\text{em}}^{\text{max}}$ (nm) | $\lambda_{\text{abs}}^{\text{max}}$ (nm) | $\lambda_{\text{em}}^{\text{max}}$ (nm) |
| Toluene | 362 | 401 | 389 | 421 | 381 | 414 |
| AcOEt | 359 | 419 | 385 | 429 | 378 | 418 |
| THF | 361 | 420 | 387 | 433 | 380 | 421 |
| CH_2Cl_2 | 365 | 428 | 389 | 449 | 384 | 434 |
| CH_3CN | 362 | 450 | 385 | 491 | 380 | 453 |
| DMSO | 365 | 454 | 391 | 492 | 384 | 454 |

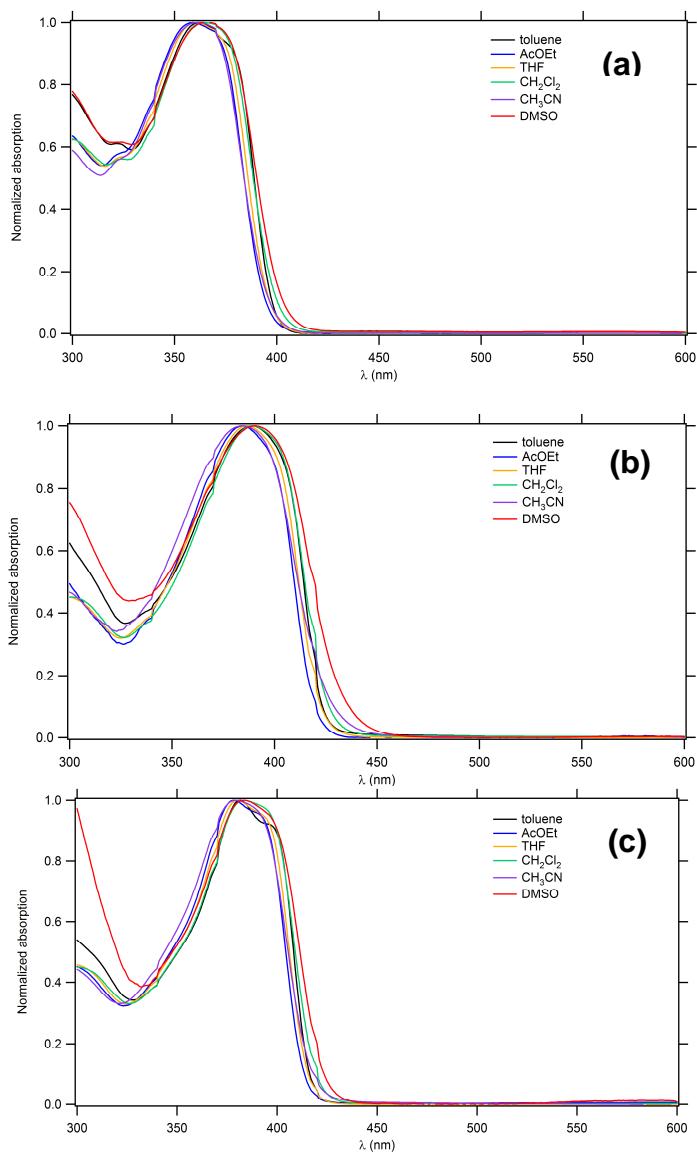


Figure S10. UV-Vis spectra of **4** (a), **5** (b) and **6** (c) in various solvents at 25 °C.

Supporting Information

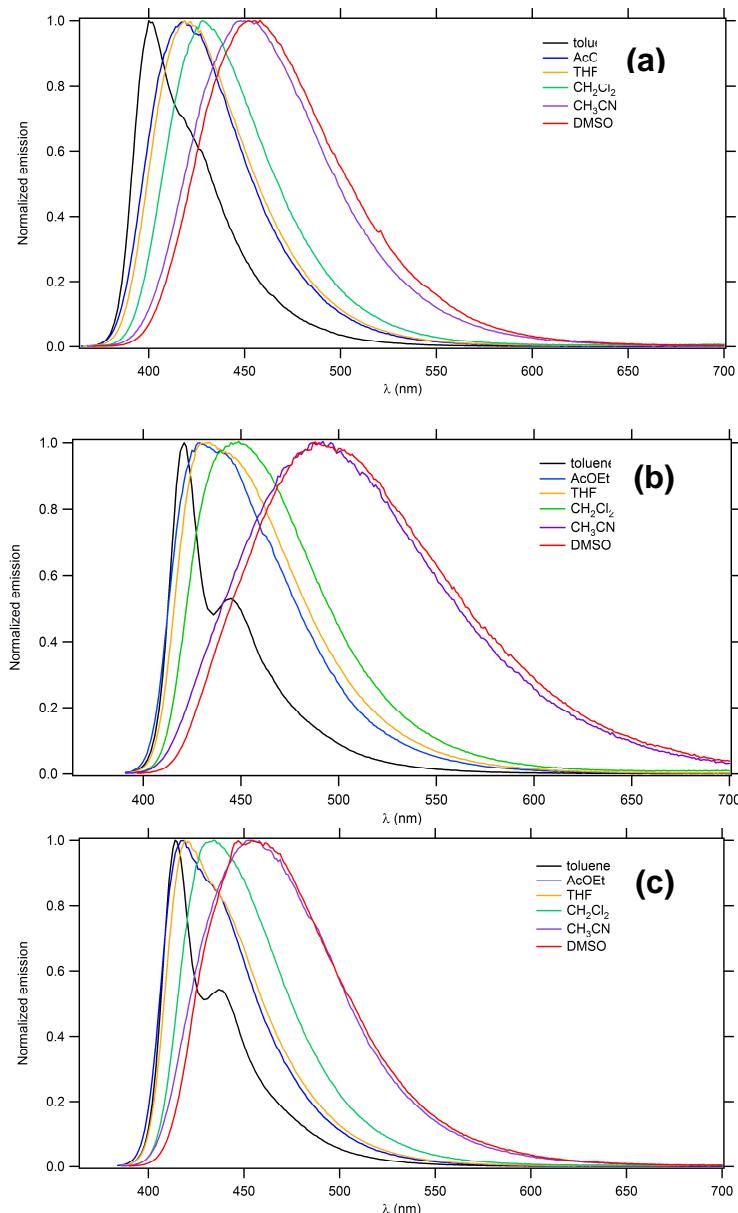


Figure S11. Emission spectra of **4** (a), **5** (b) and **6** (c) in various solvents at 25 °C.

7. Cyclic Voltammograms for 4-6

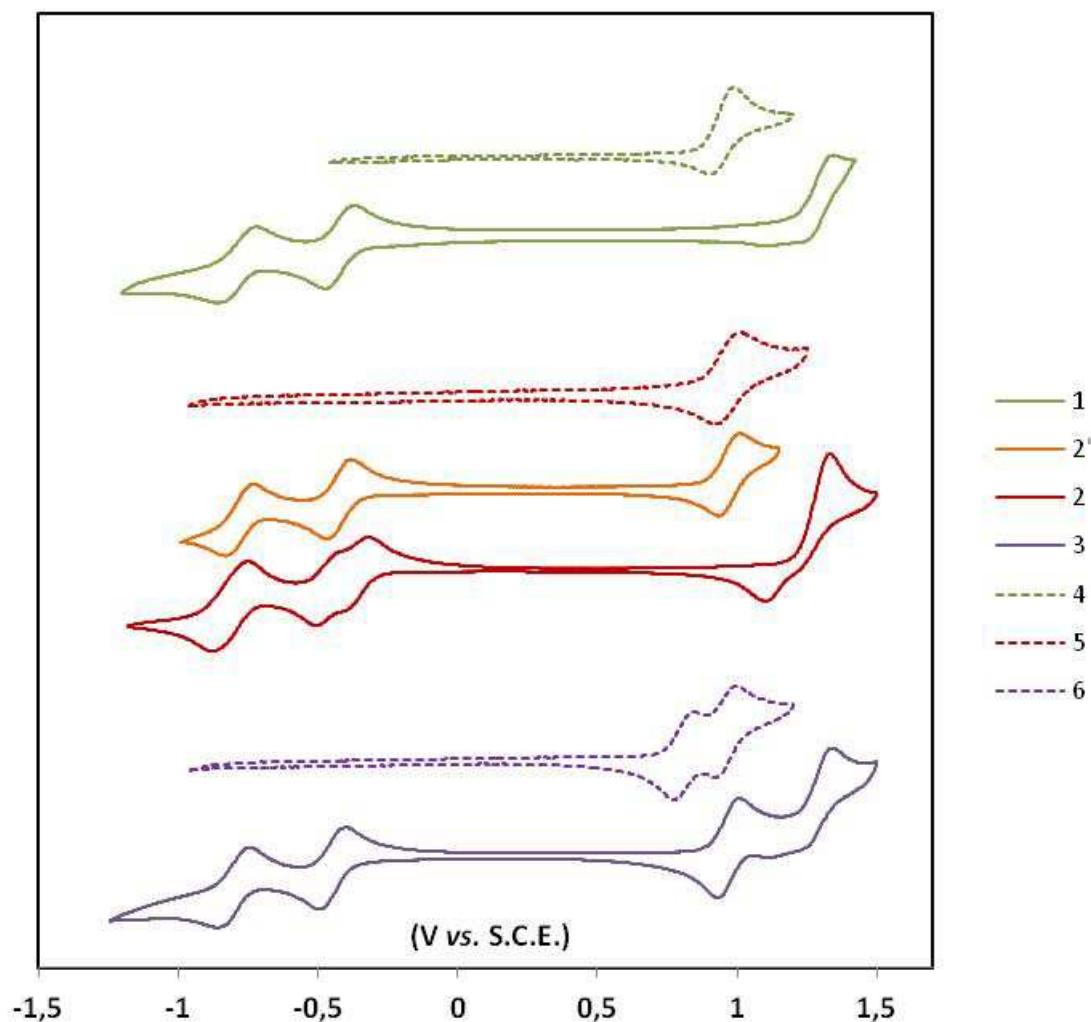
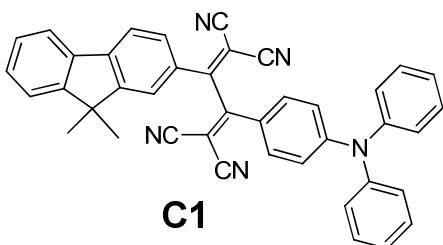


Figure S12 . Cyclic voltammograms of **1-6** and **2'** in $\text{CH}_2\text{Cl}_2/[n\text{-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M) at 25 °C at 0.1 V/s.

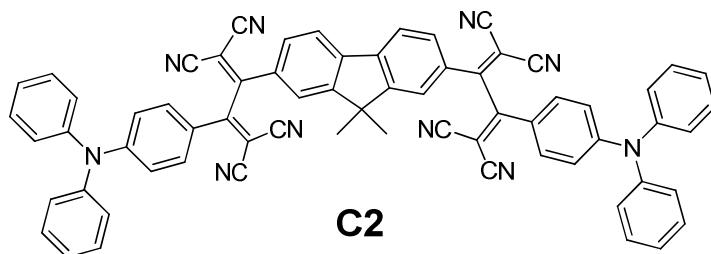
8. Cartesian Coordinates of the DFT Optimized Geometries for C1-C6



| | | | |
|---|-------------|-------------|-------------|
| C | 2.18638600 | 0.18298500 | -0.99396100 |
| C | 2.39084900 | 0.44630100 | 0.37625100 |
| C | 3.66172700 | 0.21268500 | 0.93827400 |
| C | 4.67010400 | -0.29965600 | 0.14940400 |
| C | 4.44380700 | -0.58754800 | -1.20948200 |
| C | 3.19681700 | -0.34276500 | -1.78392700 |
| H | 1.21354600 | 0.37976900 | -1.43544500 |
| H | 3.85727100 | 0.47116600 | 1.97326300 |
| H | 3.01313700 | -0.54909900 | -2.83463400 |
| C | 6.10214200 | -0.61512700 | 0.54238200 |
| C | 6.65781200 | -1.13150000 | -0.77348400 |
| C | 7.93702100 | -1.58894300 | -1.05496700 |
| C | 8.23223300 | -2.01886200 | -2.34895700 |
| C | 7.25937700 | -1.99278500 | -3.35101400 |
| C | 5.97441900 | -1.53661400 | -3.07629900 |
| C | 5.68006400 | -1.10747700 | -1.78291900 |
| H | 8.70332800 | -1.61324700 | -0.28372300 |
| H | 7.50956700 | -2.33123700 | -4.35260400 |
| H | 5.21875000 | -1.51663800 | -3.85750600 |
| C | 6.84335600 | 0.64766100 | 1.00622500 |
| H | 6.39640300 | 1.04290100 | 1.92501100 |
| H | 7.89391800 | 0.41742200 | 1.21553600 |
| H | 6.80714200 | 1.43123900 | 0.24341000 |
| C | 6.15121400 | -1.69291600 | 1.63618400 |
| H | 7.18998800 | -1.94557900 | 1.87675600 |
| H | 5.66748200 | -1.33806400 | 2.55293500 |
| H | 5.64170800 | -2.60610900 | 1.31338900 |
| C | 1.27756500 | 0.96419000 | 1.16795000 |
| C | 0.24753800 | 1.79670400 | 0.46422000 |
| C | 1.08606400 | 0.73312200 | 2.50599200 |
| C | 0.00162700 | 1.33905100 | 3.21477700 |
| C | 1.90368300 | -0.13009200 | 3.29851500 |
| N | -0.86907300 | 1.81985600 | 3.81546900 |
| N | 2.53170400 | -0.83574100 | 3.97566300 |
| C | 0.66073400 | 3.04190200 | 0.04714800 |
| C | 1.95823800 | 3.53198300 | 0.38989300 |
| C | -0.11726400 | 3.92657200 | -0.75686300 |
| N | -0.70947700 | 4.66757900 | -1.42935400 |
| N | 3.00874000 | 3.94438000 | 0.66891200 |
| C | -1.06871600 | 1.21868300 | 0.26998400 |
| C | -2.23227400 | 1.99526200 | 0.08996400 |
| C | -1.22643600 | -0.18352900 | 0.27983800 |
| C | -3.46654400 | 1.40989100 | -0.08823900 |
| H | -2.18076000 | 3.07629100 | 0.14196300 |

Supporting Information

| | | | |
|---|-------------|-------------|-------------|
| C | -2.45518900 | -0.77801900 | 0.08732900 |
| H | -0.35749800 | -0.82269800 | 0.40954900 |
| C | -3.60993600 | 0.00711800 | -0.10173200 |
| H | -4.34486900 | 2.03829400 | -0.18760500 |
| H | -2.53252700 | -1.85968700 | 0.07379300 |
| N | -4.85179200 | -0.58101200 | -0.28178900 |
| C | -5.89824500 | 0.10395600 | -0.95843700 |
| C | -7.17887500 | 0.14322900 | -0.40081400 |
| C | -5.66147300 | 0.71534900 | -2.19328900 |
| C | -8.20911200 | 0.79012700 | -1.07361300 |
| H | -7.35812200 | -0.33510300 | 0.55754500 |
| C | -6.69426200 | 1.37361300 | -2.85129400 |
| H | -4.66829600 | 0.67168800 | -2.63096200 |
| C | -7.97161300 | 1.41156800 | -2.29735500 |
| H | -9.20114000 | 0.81717700 | -0.63143600 |
| H | -6.50004500 | 1.84796100 | -3.80921900 |
| H | -8.77751400 | 1.92147200 | -2.81711900 |
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| C | -6.02079000 | -4.10021700 | -0.12467200 |
| H | -5.96781900 | -2.56706800 | -1.64104700 |
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| H | -5.92979700 | -5.42999000 | 1.56829800 |
| H | 9.23126300 | -2.37783800 | -2.58116500 |



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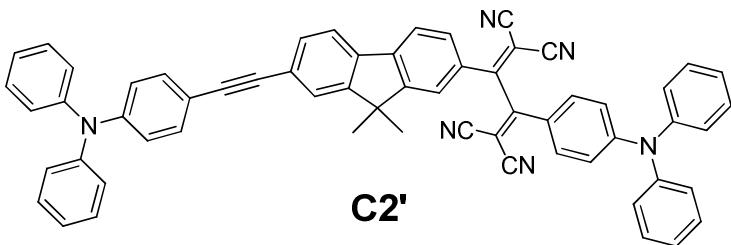
Supporting Information

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Supporting Information

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| H | 8.81098600 | 2.84107200 | 2.76365500 |
| C | 12.11305500 | 3.55871300 | 3.15678600 |
| H | 13.56017900 | 3.59692500 | 1.56164300 |
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| C | 9.35289000 | 5.46434300 | -2.09985000 |
| H | 9.28081900 | 5.17184900 | 0.03614600 |
| C | 9.41334800 | 3.46018900 | -3.43297500 |
| H | 9.42747600 | 1.60150100 | -2.34045600 |
| C | 9.39473000 | 4.85046900 | -3.34948700 |
| H | 9.33740800 | 6.54810300 | -2.02466000 |
| H | 9.45803300 | 2.97166400 | -4.40234600 |
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| C | 6.90465800 | -2.82716100 | -1.68104700 |
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| N | 8.04415700 | -3.03491600 | -1.77028500 |
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Supporting Information



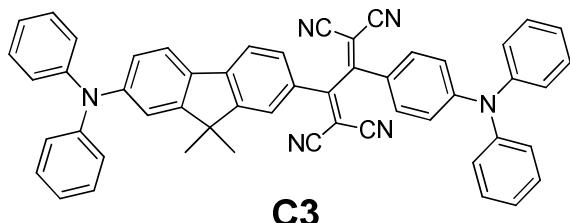
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| C | 2.95701500 | 0.98736800 | 0.10411100 |
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| H | 3.39382700 | -2.01130700 | -1.46429700 |
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| C | 0.97549900 | 3.51716000 | -0.18369200 |
| H | 0.26970200 | 4.28957500 | 0.14081100 |
| H | 1.98584200 | 3.85462800 | 0.07261200 |
| H | 0.90708800 | 3.42630100 | -1.27192200 |
| C | 0.75479700 | 2.33571800 | 2.03237300 |
| H | 1.75448000 | 2.67594100 | 2.32465200 |
| H | 0.02752600 | 3.07350100 | 2.38872100 |
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| N | -3.36991300 | 3.42938600 | 3.11063000 |
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Supporting Information

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Supporting Information

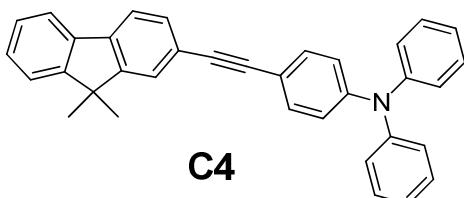
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Supporting Information

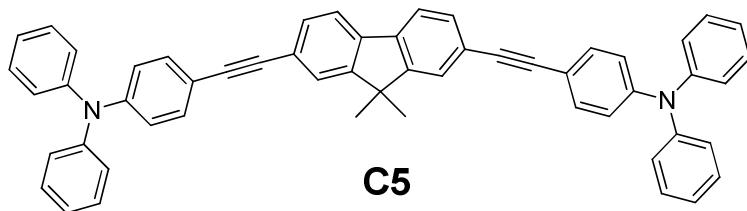
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| H | 9.17528000 | -3.12027600 | -0.98265500 |
| H | 11.21116000 | -0.57613900 | 1.81609400 |
| H | 11.01932200 | -2.76177700 | 0.64684400 |
| C | -8.14244500 | 1.34963000 | -0.95352800 |
| C | -9.48564800 | 1.34132900 | -0.56727200 |
| C | -7.81395900 | 1.45940900 | -2.30840300 |
| C | -10.48532200 | 1.44013800 | -1.52818600 |
| H | -9.73766600 | 1.25758500 | 0.48570700 |
| C | -8.82094500 | 1.54047900 | -3.26342100 |
| H | -6.76988000 | 1.48010400 | -2.60700600 |
| C | -10.15958800 | 1.53458100 | -2.87908500 |
| H | -11.52638800 | 1.43099400 | -1.21741400 |
| H | -8.55441800 | 1.62219600 | -4.31349800 |
| H | -10.94366300 | 1.60444800 | -3.62737500 |
| C | -7.24306400 | 2.10070700 | 1.18327000 |
| C | -7.52765200 | 3.46088500 | 1.03750800 |
| C | -7.10581600 | 1.55427900 | 2.46273400 |
| C | -7.67135600 | 4.26428500 | 2.16303800 |
| H | -7.63702100 | 3.87853600 | 0.04090800 |
| C | -7.23603400 | 2.36859700 | 3.58226800 |
| H | -6.89957600 | 0.49335000 | 2.57250100 |
| C | -7.52169600 | 3.72434900 | 3.43827700 |
| H | -7.89219600 | 5.32104100 | 2.04053000 |
| H | -7.12774200 | 1.93524600 | 4.57265700 |
| H | -7.63006700 | 4.35581400 | 4.31533300 |
| C | -1.96406800 | -2.67404100 | 1.71114300 |
| C | -2.39529700 | -3.02244800 | -1.63605600 |
| C | -1.15188700 | -2.61275200 | 2.88419300 |
| C | -3.21853500 | -3.33542500 | 1.89193000 |
| N | -0.53034900 | -2.57023200 | 3.86570800 |
| N | -4.23110700 | -3.87940900 | 2.06367300 |
| C | -1.25636500 | -3.88505500 | -1.61493400 |
| C | -3.18431900 | -3.10767300 | -2.82150700 |
| N | -0.33788800 | -4.59761500 | -1.60946500 |
| N | -3.78683200 | -3.19268300 | -3.81235500 |



| | | | |
|---|--------------|-------------|-------------|
| C | -3.66104200 | -1.74772700 | -0.89220100 |
| C | -3.05089600 | -0.60395200 | -0.32165100 |
| C | -3.87209700 | 0.42594000 | 0.20459800 |
| C | -5.25242100 | 0.29730800 | 0.15373600 |
| C | -5.84933800 | -0.85198800 | -0.41820000 |
| C | -5.04973100 | -1.87403400 | -0.94172000 |
| H | -3.40207700 | 1.30151300 | 0.64097700 |
| H | -5.49629700 | -2.75978700 | -1.38295200 |
| C | -6.32374100 | 1.27510400 | 0.65634400 |
| C | -7.60855400 | 0.51841800 | 0.29380500 |
| C | -8.93252700 | 0.89619300 | 0.50300400 |
| C | -9.96301000 | 0.03820500 | 0.08567600 |
| C | -9.66520800 | -1.18404000 | -0.53421600 |
| C | -8.33578500 | -1.56977500 | -0.74723700 |
| C | -7.30875300 | -0.71553900 | -0.33139800 |
| H | -9.17405200 | 1.84055400 | 0.98262000 |
| H | -10.99839600 | 0.32318300 | 0.24417200 |
| H | -10.47245400 | -1.83680500 | -0.85147200 |
| H | -8.11200000 | -2.51771300 | -1.22726600 |
| C | -1.63200500 | -0.49112200 | -0.27517300 |
| C | -0.41480200 | -0.39310800 | -0.23105100 |
| C | 1.00327900 | -0.28572700 | -0.17823400 |
| C | 1.83187200 | -1.29946500 | -0.71247100 |
| C | 1.62976500 | 0.83582200 | 0.41248000 |
| C | 3.21810500 | -1.19546700 | -0.66285800 |
| H | 1.37319100 | -2.16442100 | -1.17932500 |
| C | 3.01590600 | 0.93559100 | 0.47437300 |
| H | 1.01410100 | 1.62175200 | 0.83652800 |
| C | 3.83461400 | -0.07774200 | -0.06446800 |
| H | 3.83310700 | -1.97861700 | -1.09064900 |
| H | 3.47383700 | 1.79761500 | 0.94516200 |
| N | 5.25258300 | 0.02454100 | -0.00468800 |
| C | 5.89150400 | 1.29447900 | -0.17019100 |
| C | 5.46756300 | 2.18101400 | -1.17750700 |
| C | 6.95630200 | 1.66935400 | 0.66969600 |
| C | 6.09202700 | 3.42141000 | -1.33078600 |
| H | 4.65426300 | 1.89334800 | -1.83428600 |
| C | 7.58577600 | 2.90486100 | 0.49815200 |
| H | 7.28310800 | 0.99196900 | 1.45052400 |
| C | 7.15605700 | 3.78994700 | -0.49825500 |
| H | 5.75430100 | 4.09487800 | -2.11233600 |
| H | 8.40572300 | 3.18066500 | 1.15394300 |
| H | 7.64298600 | 4.75125900 | -0.62445800 |
| C | 6.05025400 | -1.14128400 | 0.22579000 |
| C | 5.66960100 | -2.08588400 | 1.19694500 |
| C | 7.22927500 | -1.35320500 | -0.51229200 |
| C | 6.45047900 | -3.22366600 | 1.41486600 |

Supporting Information

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|---|-------------|-------------|-------------|
| H | 4.76712900 | -1.92273800 | 1.77513900 |
| C | 8.01279200 | -2.48557800 | -0.27565100 |
| H | 7.52331700 | -0.63104700 | -1.26554300 |
| C | 7.62745400 | -3.42937500 | 0.68438600 |
| H | 6.14453600 | -3.94363200 | 2.16751200 |
| H | 8.91967900 | -2.63607100 | -0.85301200 |
| H | 8.23488300 | -4.31085900 | 0.86087000 |
| H | -3.02792000 | -2.53173100 | -1.29307300 |
| C | -6.24082900 | 2.63431700 | -0.08605600 |
| H | -7.05383600 | 3.29667100 | 0.23364100 |
| H | -5.28978100 | 3.13463100 | 0.13068200 |
| H | -6.31690300 | 2.49379800 | -1.16893100 |
| C | -6.21158400 | 1.50056600 | 2.18638200 |
| H | -6.26914600 | 0.55045100 | 2.72684400 |
| H | -5.25886400 | 1.98197700 | 2.43603200 |
| H | -7.02235100 | 2.14827400 | 2.53976900 |



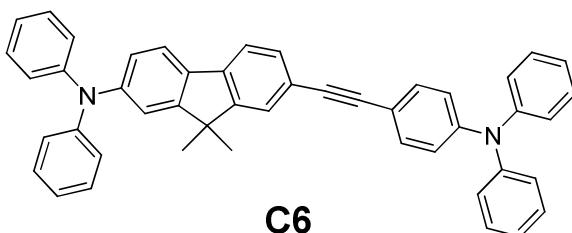
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|---|-------------|-------------|-------------|
| C | 0.76023700 | -2.38676800 | -0.09432400 |
| C | 1.28645800 | -1.07362500 | -0.02219300 |
| C | 0.39131600 | 0.02544600 | 0.03924000 |
| C | -0.97664800 | -0.20123100 | 0.02672500 |
| C | -1.49008100 | -1.51961200 | -0.04539500 |
| C | -0.61650500 | -2.61207800 | -0.10562900 |
| H | 0.79659500 | 1.03079900 | 0.09318400 |
| H | -0.99763200 | -3.62713600 | -0.16140500 |
| C | -2.11644500 | 0.82586800 | 0.07900800 |
| C | -3.34499700 | -0.09329200 | 0.02764100 |
| C | -4.68681900 | 0.25810900 | 0.03817400 |
| C | -5.67880600 | -0.75511400 | -0.01258500 |
| C | -5.27446200 | -2.11160800 | -0.07799200 |
| C | -3.92383400 | -2.46011900 | -0.09865100 |
| C | -2.95368700 | -1.45250500 | -0.04359600 |
| H | -4.99735000 | 1.29727500 | 0.08296800 |
| H | -6.03587900 | -2.88334800 | -0.11053400 |
| H | -3.63754700 | -3.50611900 | -0.15191300 |
| C | 2.69402100 | -0.85901300 | -0.01450900 |
| C | 3.90117700 | -0.66871300 | -0.01090000 |
| C | 5.30741200 | -0.45060300 | -0.01102100 |
| C | 6.21185200 | -1.51993800 | -0.20607400 |
| C | 5.84631400 | 0.84248800 | 0.18142300 |
| C | 7.58631700 | -1.30636000 | -0.21749700 |
| H | 5.82106000 | -2.51926700 | -0.36459200 |
| C | 7.22089800 | 1.05586300 | 0.18441400 |

Supporting Information

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|---|--------------|-------------|-------------|
| H | 5.17185800 | 1.67649300 | 0.34296000 |
| C | 8.11541500 | -0.01457800 | -0.01973800 |
| H | 8.25954500 | -2.13898800 | -0.38459200 |
| H | 7.61122200 | 2.05358700 | 0.34756700 |
| N | 9.52129800 | 0.20384300 | -0.02734500 |
| C | 10.06413300 | 1.39963700 | -0.59624700 |
| C | 9.57026900 | 1.89988100 | -1.81548000 |
| C | 11.10595600 | 2.08565300 | 0.05478700 |
| C | 10.10393800 | 3.06927100 | -2.36301500 |
| H | 8.77444800 | 1.37019000 | -2.32690700 |
| C | 11.64485700 | 3.24493100 | -0.50890000 |
| H | 11.48621600 | 1.70727800 | 0.99690200 |
| C | 11.14560600 | 3.74662200 | -1.71714300 |
| H | 9.71328400 | 3.44318000 | -3.30431600 |
| H | 12.44821600 | 3.76358700 | 0.00496400 |
| H | 11.56193300 | 4.65069700 | -2.14898300 |
| C | 10.40610200 | -0.77512700 | 0.52758400 |
| C | 10.11001000 | -1.38962500 | 1.75831700 |
| C | 11.58724300 | -1.12956700 | -0.14983700 |
| C | 10.97611900 | -2.34734100 | 2.29201200 |
| H | 9.20566600 | -1.11304000 | 2.28853900 |
| C | 12.45579400 | -2.07607400 | 0.39960800 |
| H | 11.81678800 | -0.66255100 | -1.10097700 |
| C | 12.15474700 | -2.69378500 | 1.61966000 |
| H | 10.73498400 | -2.81309700 | 3.24245100 |
| H | 13.36335700 | -2.34003700 | -0.13432600 |
| H | 12.82822000 | -3.43311100 | 2.04037300 |
| C | -7.06097100 | -0.41419400 | 0.00243500 |
| C | -8.24492700 | -0.11927100 | 0.01577800 |
| N | -9.55846100 | 0.20631600 | 0.03094100 |
| C | -9.95033900 | 1.50196500 | 0.51927300 |
| C | -11.03543300 | 2.18579800 | -0.05488100 |
| C | -9.21357900 | 2.10703700 | 1.54988100 |
| C | -11.38538100 | 3.45381400 | 0.41609800 |
| H | -11.59233500 | 1.73250100 | -0.86612800 |
| C | -9.56610800 | 3.38028700 | 2.00508300 |
| H | -8.37276200 | 1.57894800 | 1.98494100 |
| C | -10.65504700 | 4.05912800 | 1.44613200 |
| H | -12.22389800 | 3.97469500 | -0.03524200 |
| H | -8.99091000 | 3.83768500 | 2.80383200 |
| H | -10.92834200 | 5.04596400 | 1.80440600 |
| C | -10.52049500 | -0.75446200 | -0.44119500 |
| C | -10.17575900 | -1.62380000 | -1.48821900 |
| C | -11.78407300 | -0.86016200 | 0.16433300 |
| C | -11.09121400 | -2.58328100 | -1.92869900 |
| H | -9.19700500 | -1.54387200 | -1.94732200 |
| C | -12.69542900 | -1.81582800 | -0.29224400 |
| H | -12.04508200 | -0.20702800 | 0.98835100 |
| C | -12.35655900 | -2.68229300 | -1.33877400 |
| H | -10.81484700 | -3.24928900 | -2.73991600 |
| H | -13.66823200 | -1.89115400 | 0.18326100 |
| H | -13.06643400 | -3.42571100 | -1.68563900 |
| H | 1.44935500 | -3.22297700 | -0.14085700 |
| C | -2.07224800 | 1.78058800 | -1.14212500 |
| H | -1.15506000 | 2.38077600 | -1.12780800 |
| H | -2.10048900 | 1.21712300 | -2.08007300 |

Supporting Information

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|---|-------------|------------|-------------|
| H | -2.92741000 | 2.46627000 | -1.12566300 |
| C | -2.07965800 | 1.64676200 | 1.39393600 |
| H | -2.93787600 | 2.32687100 | 1.44565100 |
| H | -2.10863300 | 0.98787500 | 2.26751600 |
| H | -1.16499900 | 2.24872600 | 1.44607100 |

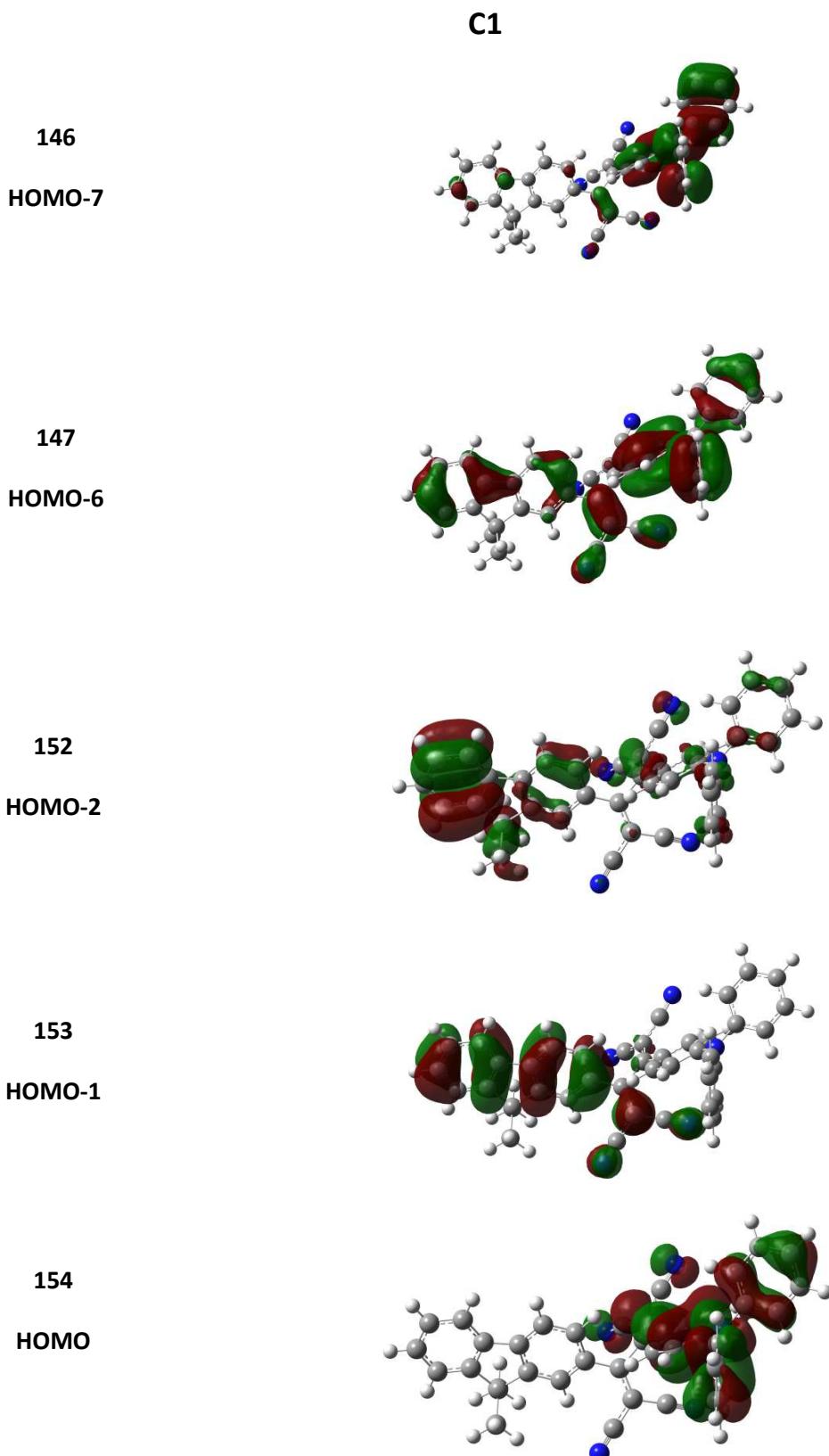


| | | | |
|---|-------------|-------------|-------------|
| C | -0.23466100 | -1.82555300 | -1.30016700 |
| C | 0.33088000 | -0.76186300 | -0.55555100 |
| C | -0.53122600 | 0.16378900 | 0.08739000 |
| C | -1.90528000 | 0.01391900 | -0.02269500 |
| C | -2.45844400 | -1.05519600 | -0.76993400 |
| C | -1.61776500 | -1.97458300 | -1.40848700 |
| H | -0.09587600 | 0.97803700 | 0.65801000 |
| H | -2.02868000 | -2.79873700 | -1.98356300 |
| C | -3.01377800 | 0.88646400 | 0.58304900 |
| C | -4.26935900 | 0.16229500 | 0.07764100 |
| C | -5.60051500 | 0.47863900 | 0.31466100 |
| C | -6.61596100 | -0.32607400 | -0.24727400 |
| C | -6.26358000 | -1.44140100 | -1.03576900 |
| C | -4.92371400 | -1.76606800 | -1.25909400 |
| C | -3.91967800 | -0.96355600 | -0.70588800 |
| H | -5.87591800 | 1.33078300 | 0.92657100 |
| H | -7.04855800 | -2.04790400 | -1.47237500 |
| H | -4.67491400 | -2.62846300 | -1.86996600 |
| C | 1.74424800 | -0.62356200 | -0.45207900 |
| C | 2.95652600 | -0.50089500 | -0.35860000 |
| C | 4.36835600 | -0.35950100 | -0.24966800 |
| C | 5.24489200 | -1.27666100 | -0.87428400 |
| C | 4.94064100 | 0.70296600 | 0.48743600 |
| C | 6.62512700 | -1.13538200 | -0.77275700 |
| H | 4.82846700 | -2.09443900 | -1.45250900 |
| C | 6.32048200 | 0.83854200 | 0.60038100 |
| H | 4.28750400 | 1.41332900 | 0.98275300 |
| C | 7.18709300 | -0.07675700 | -0.03073900 |
| H | 7.27751600 | -1.84279200 | -1.27135300 |
| H | 6.73645200 | 1.65308100 | 1.18187900 |
| N | 8.59905800 | 0.06566000 | 0.07855800 |
| C | 9.19450300 | 1.36689800 | 0.06498200 |
| C | 8.75663200 | 2.34270800 | -0.84968900 |
| C | 10.23045000 | 1.68420300 | 0.96275200 |
| C | 9.33995100 | 3.61223500 | -0.85611800 |
| H | 7.96474400 | 2.10081300 | -1.54955800 |
| C | 10.81923000 | 2.95103000 | 0.93773600 |
| H | 10.56689200 | 0.93762400 | 1.67318700 |

Supporting Information

| | | | |
|---|--------------|-------------|-------------|
| C | 10.37616800 | 3.92359700 | 0.03288500 |
| H | 8.99232500 | 4.35464900 | -1.56775400 |
| H | 11.61748200 | 3.18152200 | 1.63638400 |
| H | 10.83139800 | 4.90837000 | 0.02039200 |
| C | 9.43301100 | -1.09098800 | 0.19891300 |
| C | 9.06463000 | -2.15201600 | 1.04682800 |
| C | 10.63581100 | -1.17846900 | -0.52600200 |
| C | 9.88191600 | -3.27981400 | 1.15721200 |
| H | 8.14294400 | -2.08643800 | 1.61394000 |
| C | 11.45495100 | -2.30287200 | -0.39643600 |
| H | 10.92056400 | -0.36655300 | -1.18555700 |
| C | 11.08264800 | -3.36146000 | 0.44120200 |
| H | 9.58506400 | -4.09025100 | 1.81564500 |
| H | 12.37989800 | -2.35628300 | -0.96219400 |
| H | 11.71797700 | -4.23595300 | 0.53482800 |
| N | -7.98988300 | -0.01100000 | -0.01912700 |
| C | -8.42487500 | 1.35040400 | -0.05308300 |
| C | -9.33404800 | 1.83383100 | 0.90663700 |
| C | -7.94904800 | 2.22655100 | -1.04683600 |
| C | -9.76117100 | 3.16340600 | 0.86475300 |
| H | -9.69926500 | 1.16604800 | 1.67867000 |
| C | -8.36919400 | 3.55872000 | -1.07082300 |
| H | -7.25589800 | 1.85813100 | -1.79465800 |
| C | -9.27960600 | 4.03542100 | -0.11952000 |
| H | -10.46241200 | 3.52115800 | 1.61234400 |
| H | -7.99394200 | 4.22156400 | -1.84442400 |
| H | -9.60873300 | 5.06895800 | -0.14513500 |
| C | -8.93147000 | -1.05418300 | 0.24221100 |
| C | -10.21450000 | -1.01856200 | -0.33601500 |
| C | -8.58936100 | -2.13150300 | 1.08147300 |
| C | -11.13434200 | -2.03625600 | -0.07159200 |
| H | -10.48244300 | -0.19599800 | -0.98930300 |
| C | -9.51043500 | -3.15275200 | 1.32684500 |
| H | -7.60566200 | -2.16164600 | 1.53600500 |
| C | -10.78882100 | -3.11113700 | 0.75668400 |
| H | -12.11950300 | -1.99453400 | -0.52583500 |
| H | -9.23133800 | -3.97638700 | 1.97671600 |
| H | -11.50366700 | -3.90294200 | 0.95469100 |
| H | 0.42874100 | -2.53035200 | -1.78955800 |
| C | -2.94741700 | 2.33991300 | 0.04608300 |
| H | -2.98880900 | 2.35532000 | -1.04766600 |
| H | -3.78645200 | 2.93060200 | 0.43181600 |
| H | -2.01616900 | 2.82395600 | 0.36243100 |
| C | -2.94617700 | 0.89289800 | 2.13209600 |
| H | -2.99260600 | -0.12568800 | 2.53009300 |
| H | -2.01232600 | 1.35438200 | 2.47349300 |
| H | -3.78135100 | 1.46621900 | 2.55104600 |

9. Frontier MOs in C1-C6



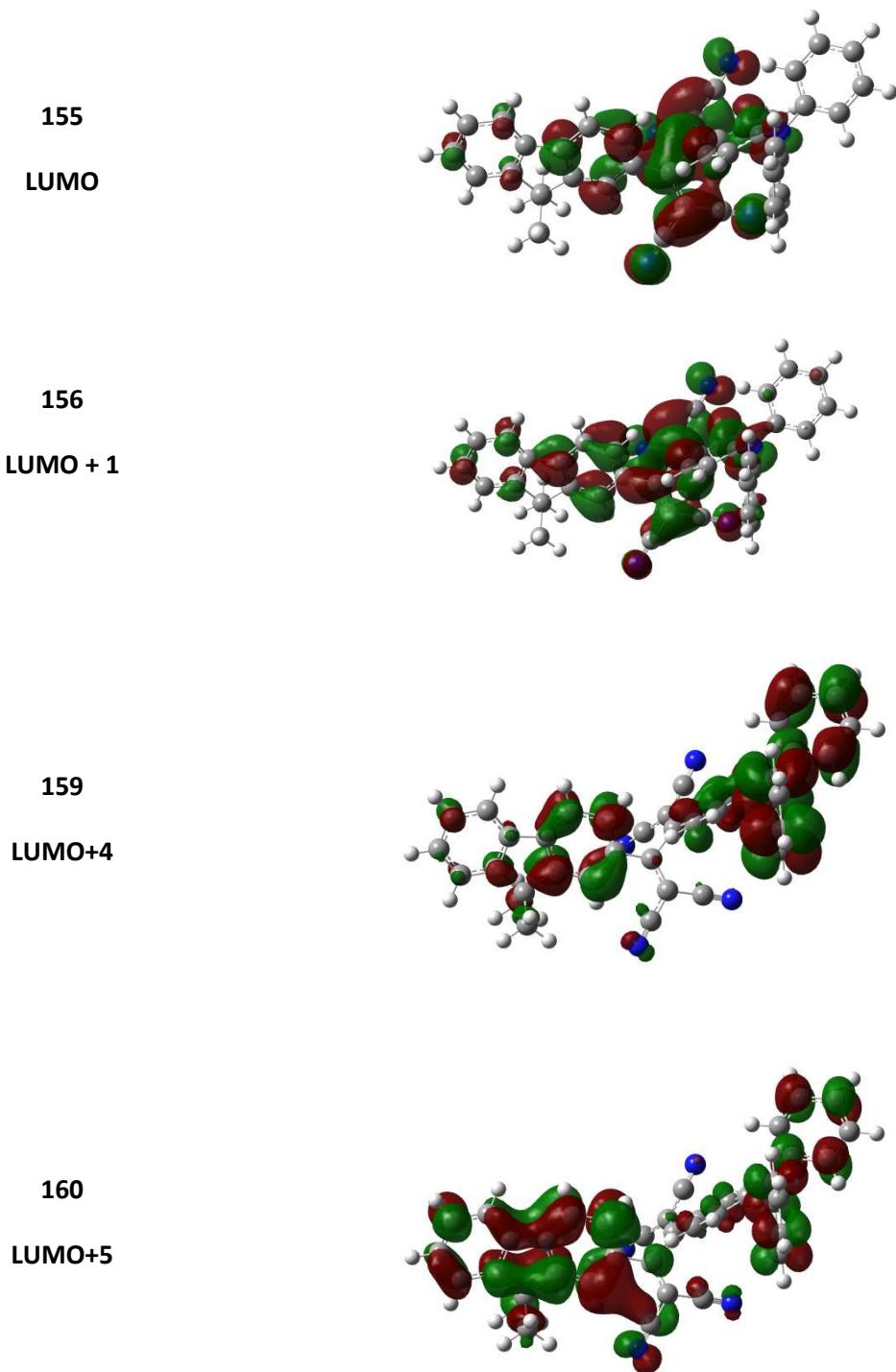
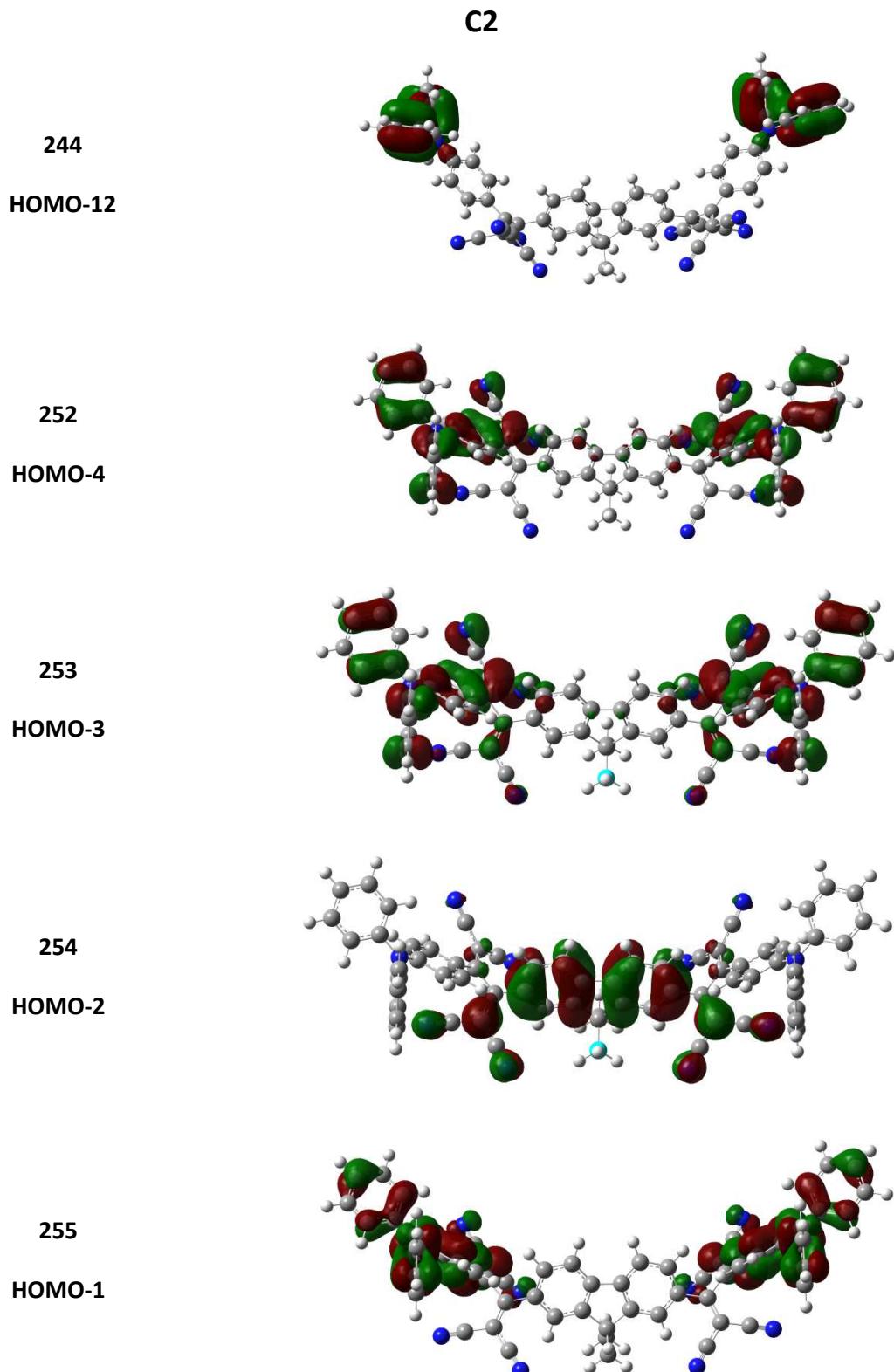
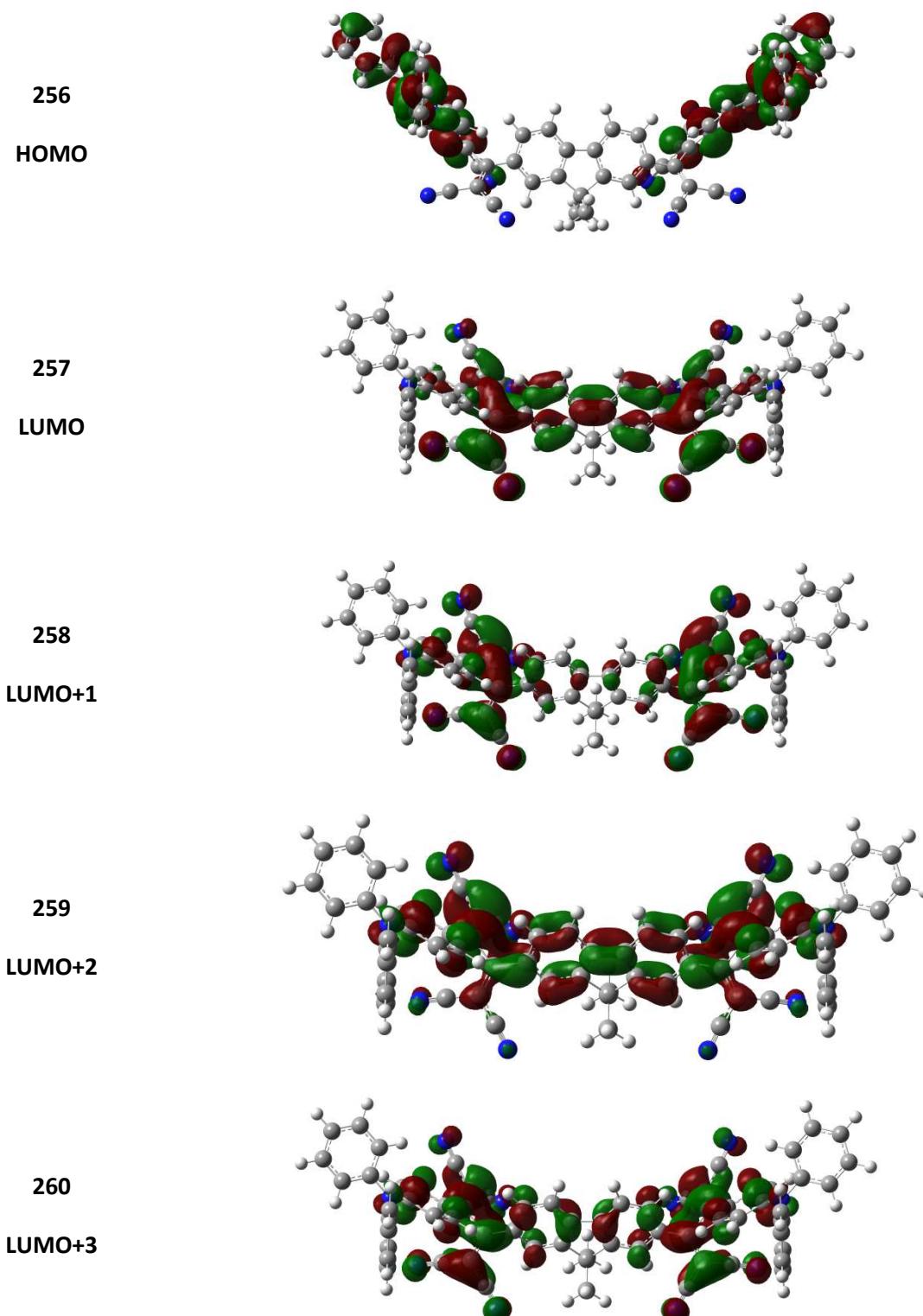


Figure S13. Frontier MOs of **C1**. Contour values are $\pm 0.02 \text{ (e/bohr}^3\text{)}^{1/2}$.





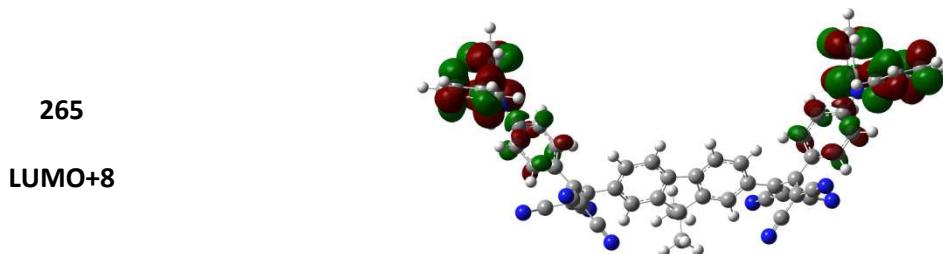
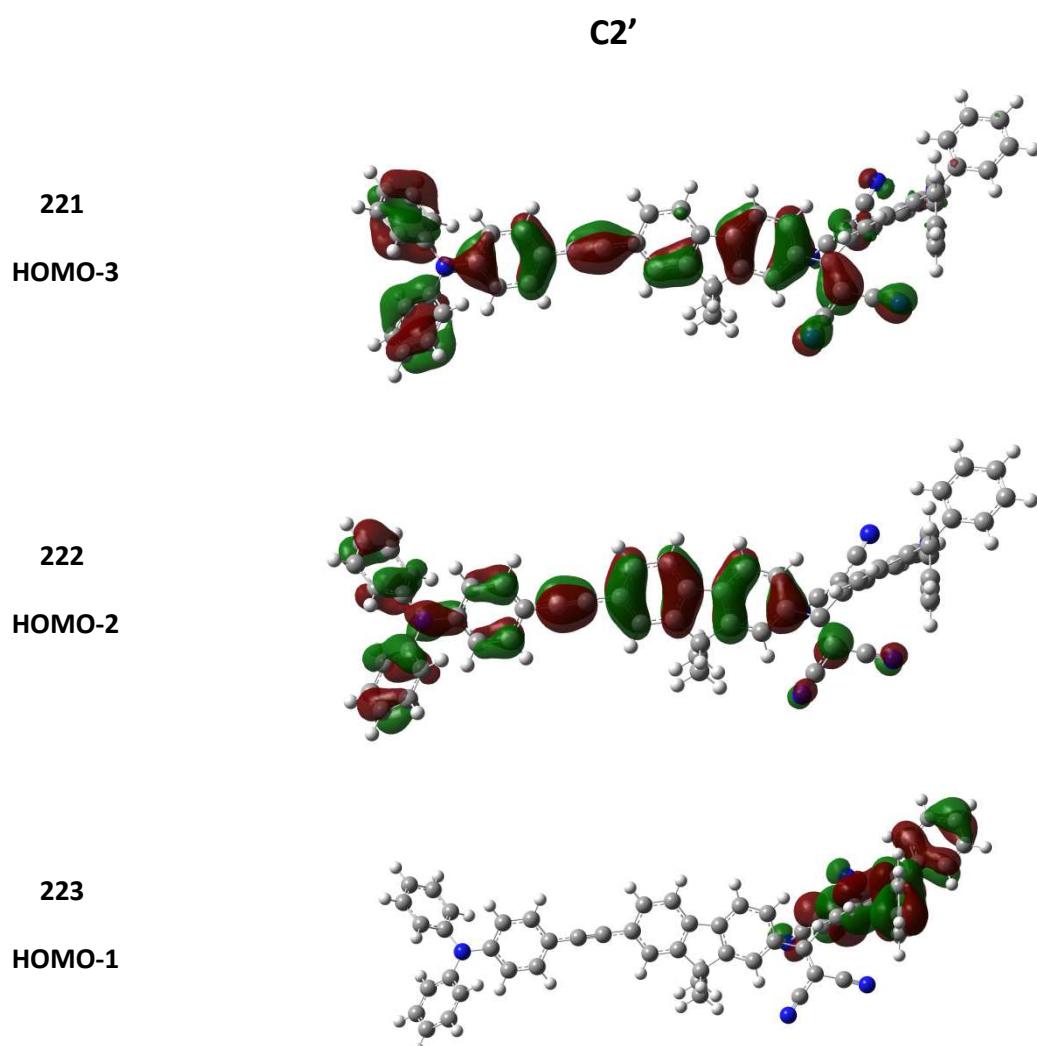
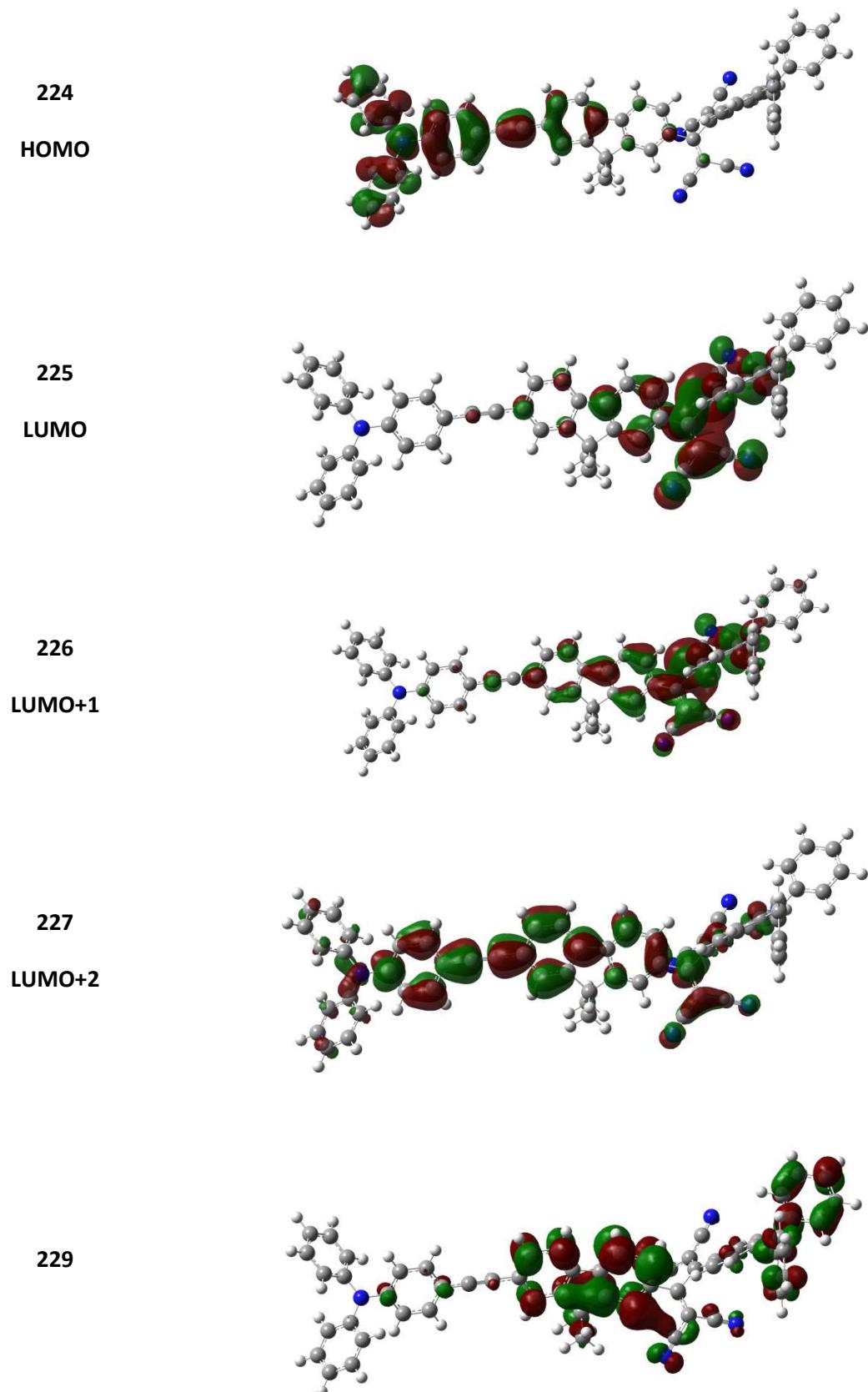
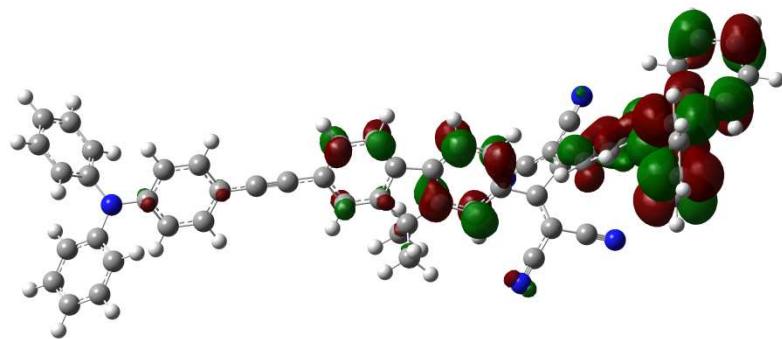


Figure S14. Frontier MOs of **C2**. Contour values are ± 0.02 ($e/\text{bohr}^3\right)^{1/2}$.

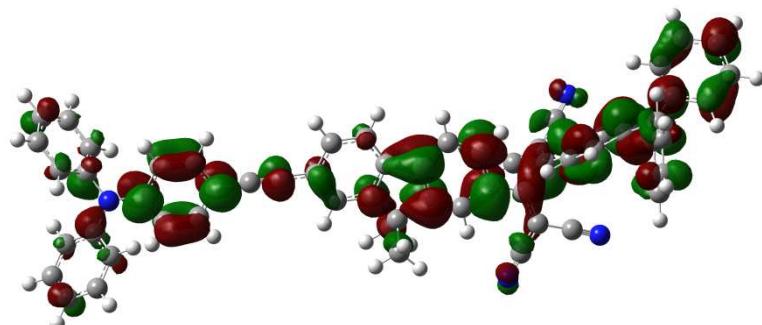




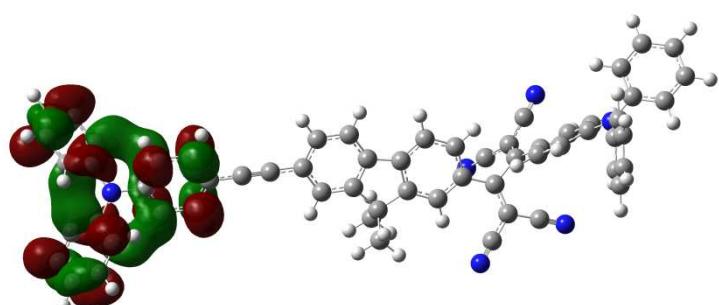
230



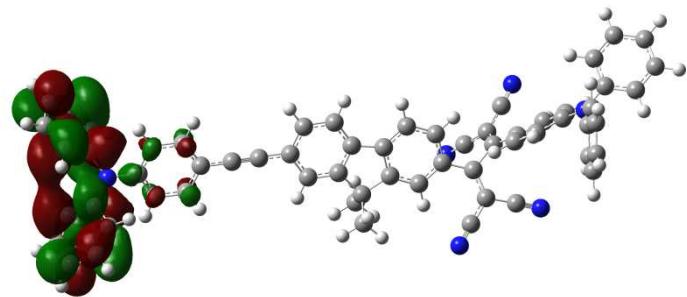
231



232



233



234

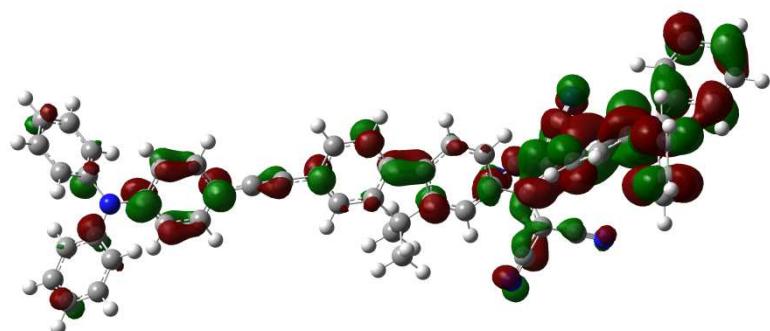
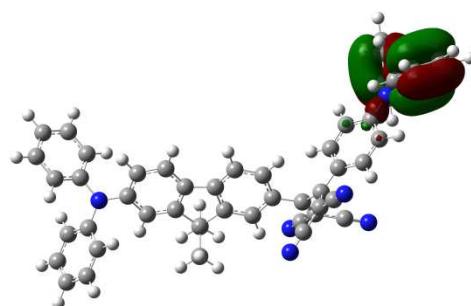


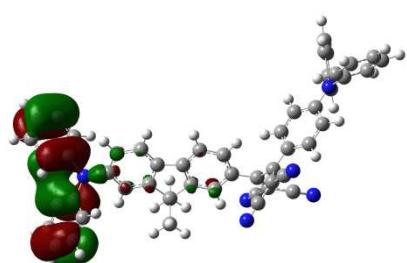
Figure S15. Frontier MOs of **C2'**. Contour values are ± 0.02 (e/bohr^3) $^{1/2}$.

C3

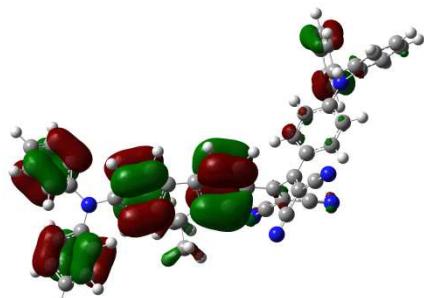
186



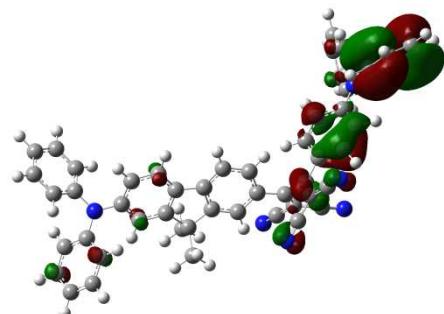
188



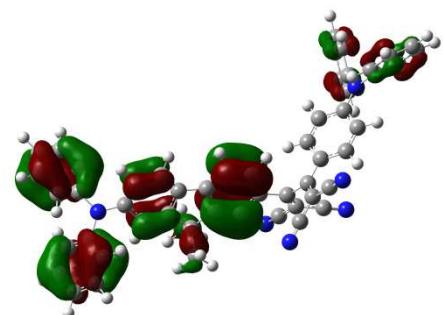
190



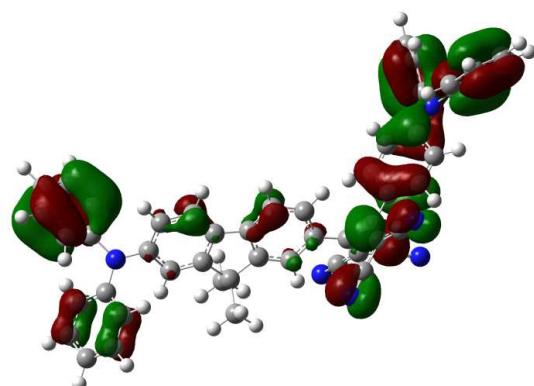
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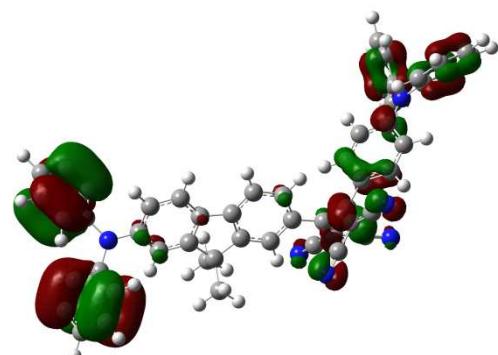
192



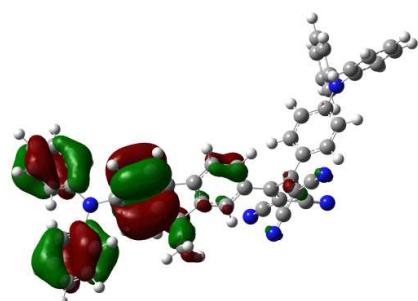
193



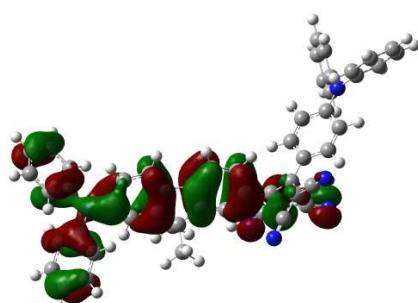
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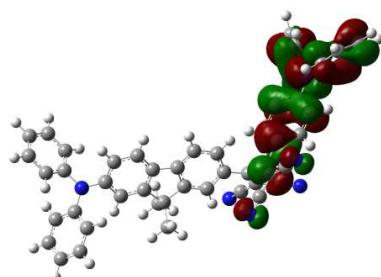
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196

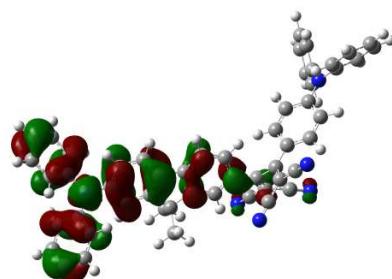


197



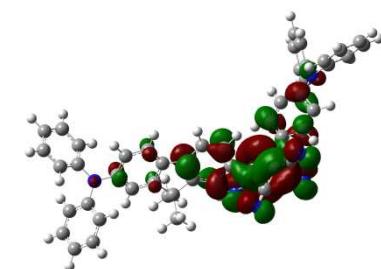
198

HOMO



199

LUMO



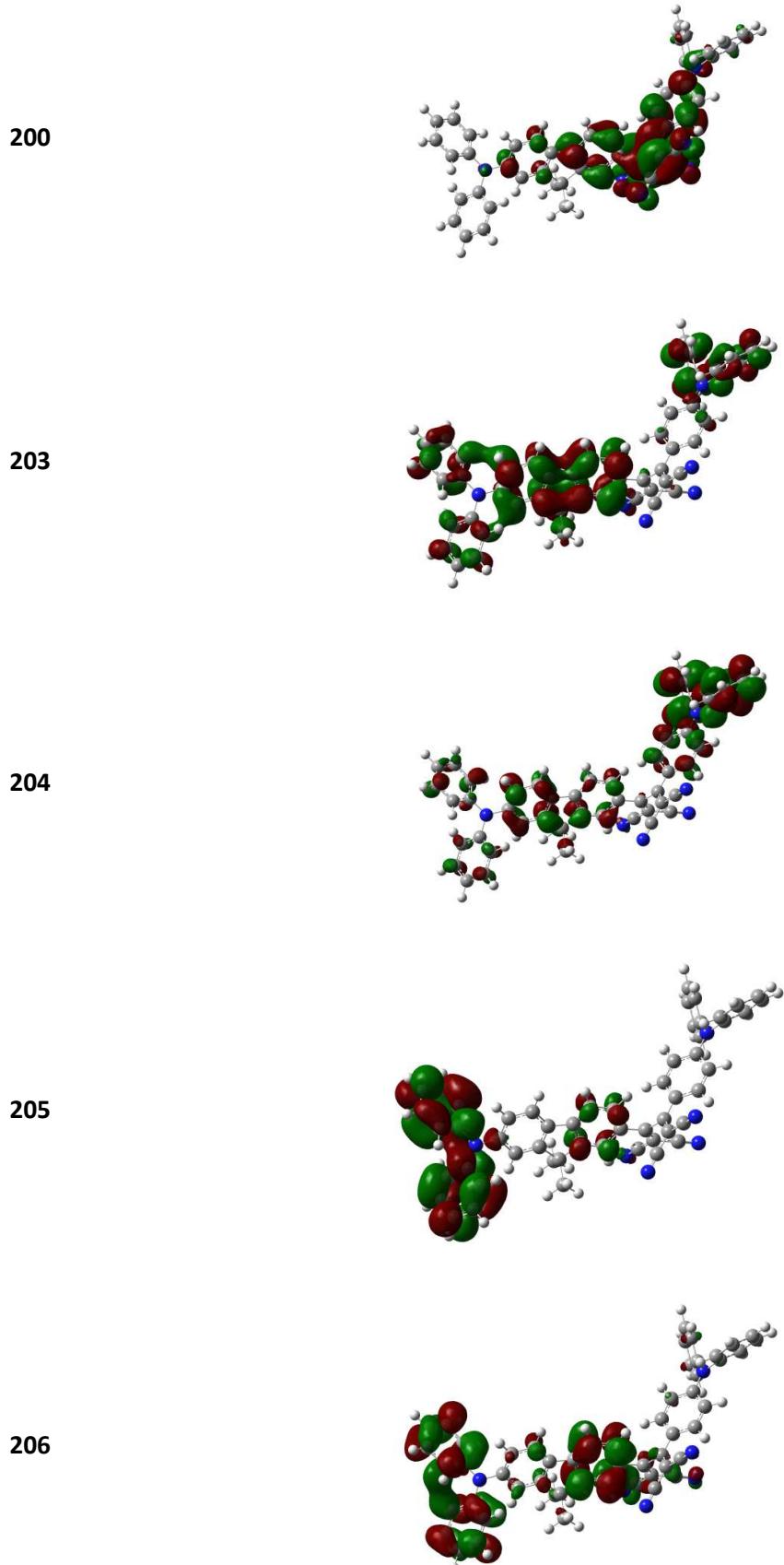


Figure S16. Frontier MOs of **C3**. Contour values are ± 0.02 (e/bohr^3) $^{1/2}$.

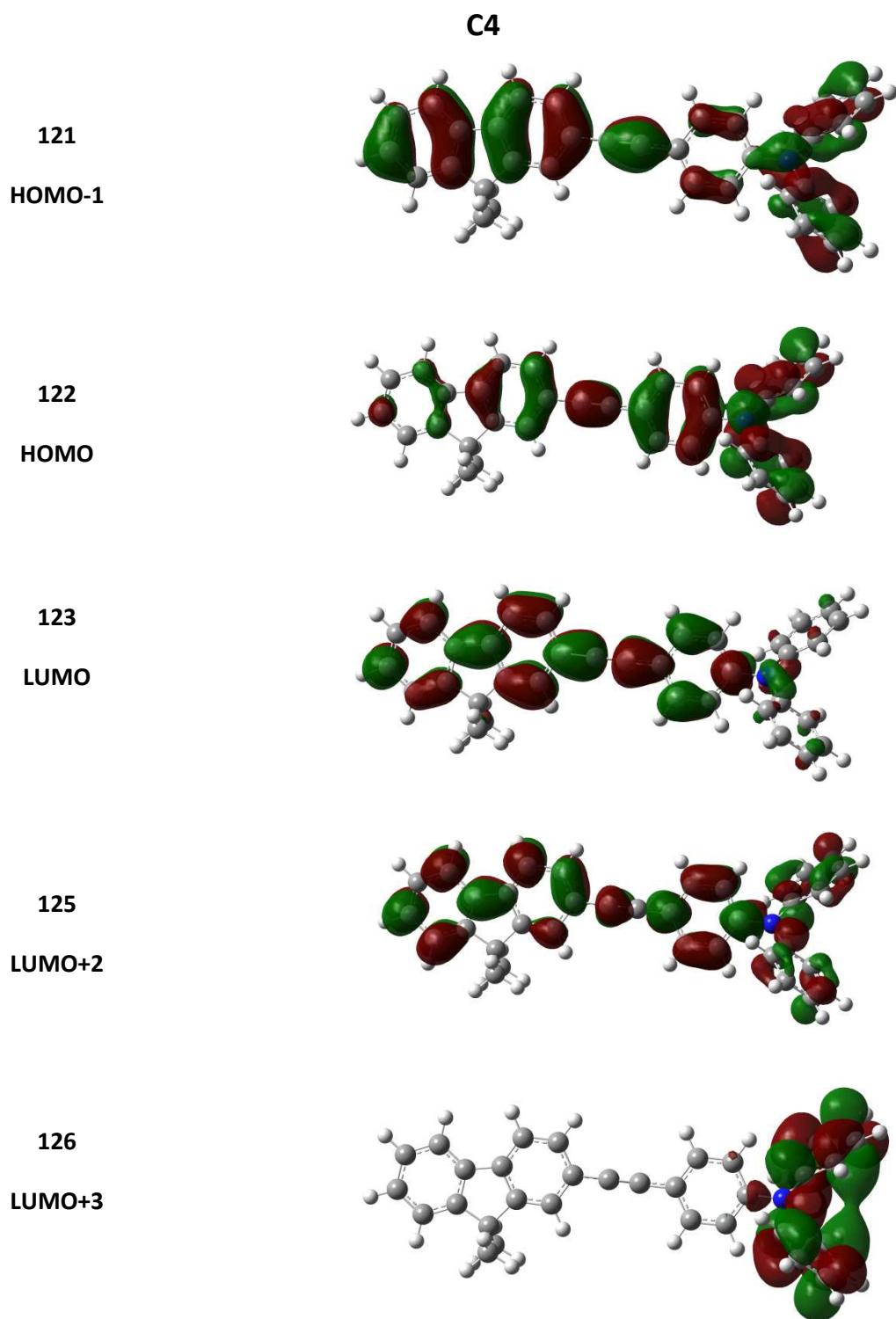
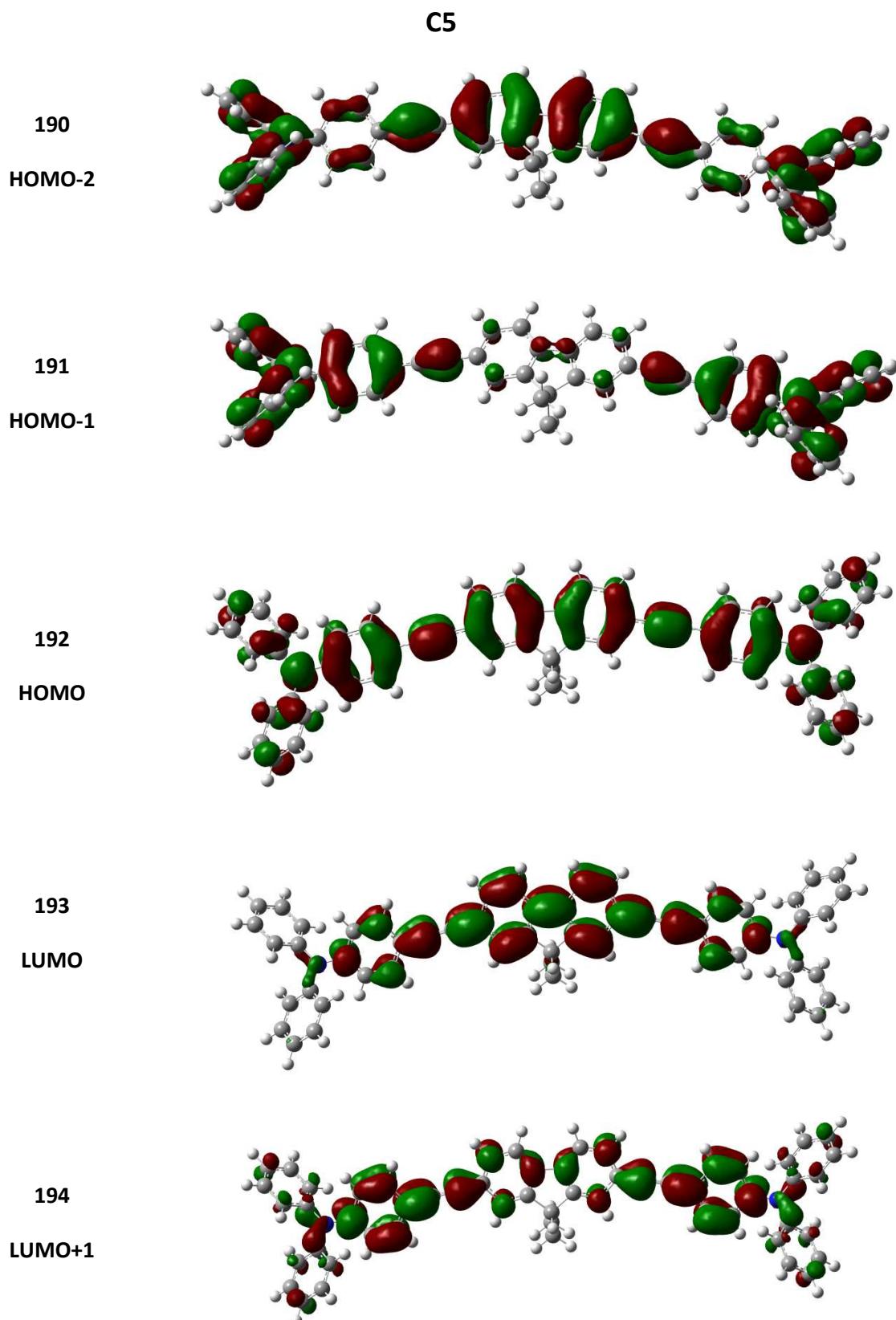


Figure S17. Frontier MOs of **C4**. Contour values are ± 0.02 (e/bohr^3) $^{1/2}$.



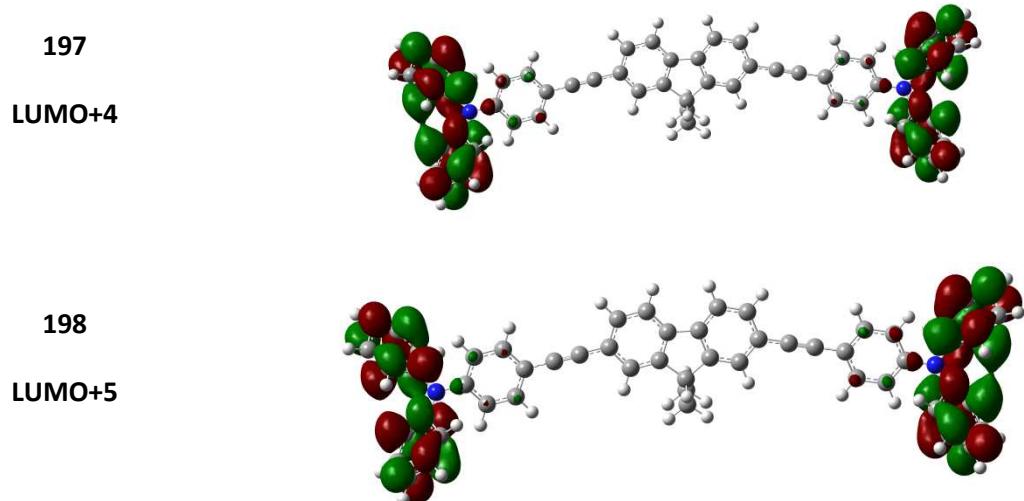
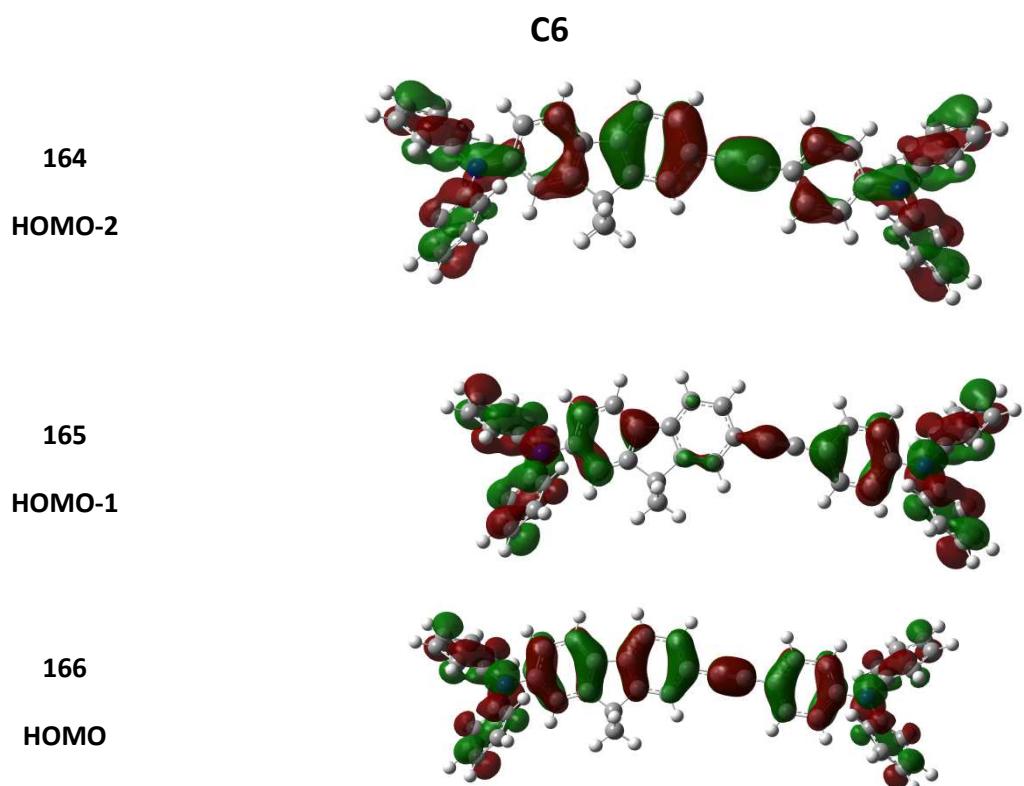


Figure S18. Frontier MOs of **C5**. Contour values are ± 0.02 ($e/\text{bohr}^3\right)^{1/2}$.



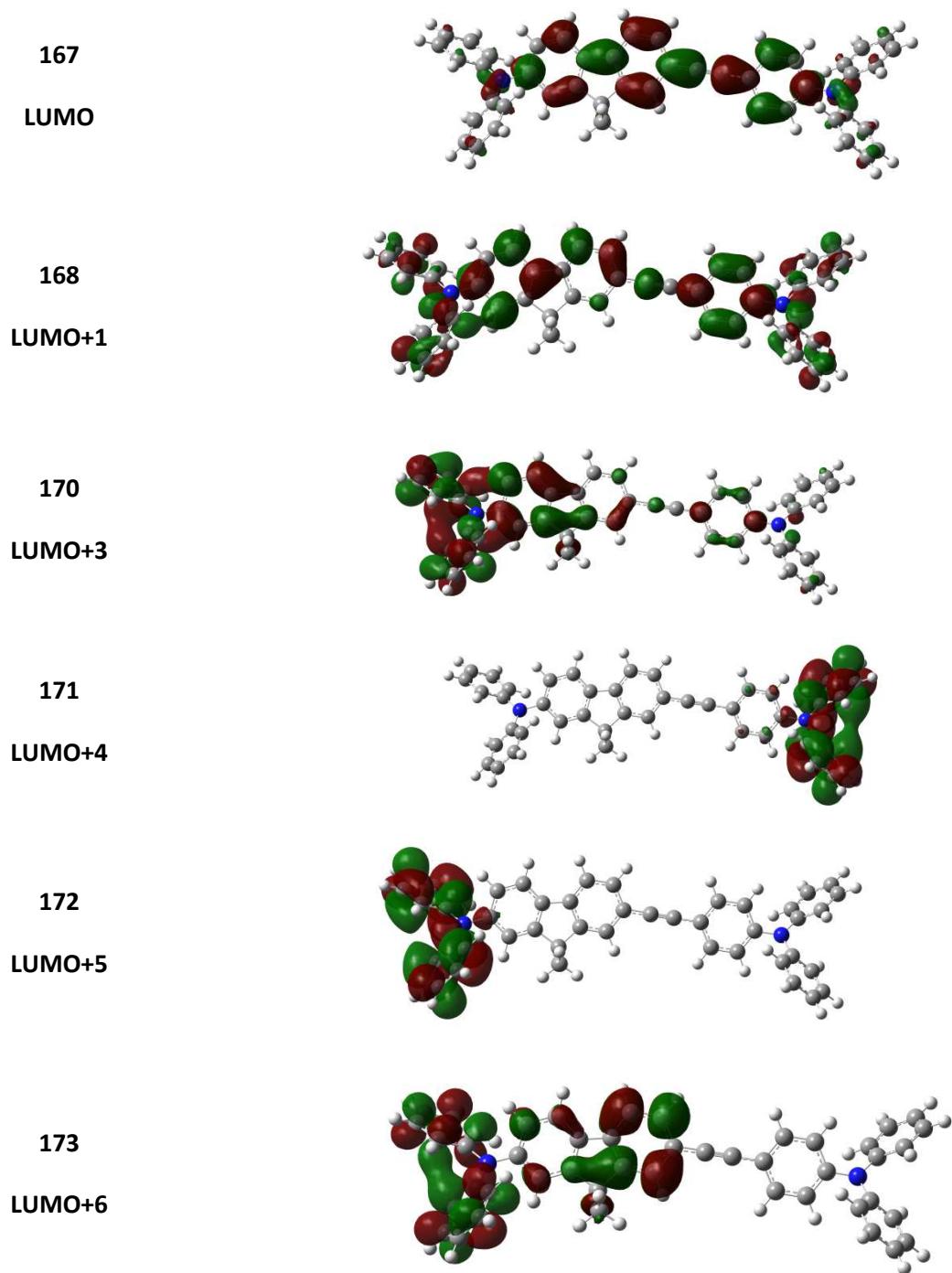


Figure S19. Frontier MOs of **C6**. Contour values are $\pm 0.02 \text{ (e/bohr}^3)^{1/2}$.

10. Experimentally Observed (CH_2Cl_2) and Computed (Vacuum) Singlet Lowest-lying Transitions for 1-6 and C1-C6, respectively

Table S4. Experimental vs. Computed ^[a] (PBE0 / 6-31G) Values (nm). Energy and Composition of the First Singlet Excited States (Wavelength, Oscillator Strength f , Transition Percentage)

| Cmpd | Experimental | Calculated ^[c] | Composition | | Major Assignment ^[e] |
|----------|--|--|--------------|---|--|
| | $\lambda_{\max} [\text{\AA}]$ ^[b] | $\lambda_{\max} [\text{f}^{\text{[d]}}]$ | | | |
| 4 | 365 [55.1] | 383 [1.49] | 122 (97%) | → | 123 $(\pi^*)_{\text{Flu}} \leftarrow (\pi)_{\text{PhNPh}_2}$ |
| | 324 [30.1] | 306 [0.43] | 121 (94%) | → | 123 $(\pi^*)_{\text{Flu/Ph}}$ $\leftarrow (\pi)_{\text{Flu/NPh}_3}$ |
| | 302 [32.5] | 301 [0.19] | 122 (94%) | → | 126 $(\pi^*)_{\text{NPh}} \leftarrow (\pi)_{\text{PhNPh}_2}$ |
| 5 | 390 [126.8] | 427 [2.90] | 192 (95%) | → | 193 $(\pi^*)_{\text{Flu}} \leftarrow (\pi)_{\text{Flu/NPh}_3}$ |
| | / | 322 [0.16] | 191 (95%) | → | 194 $(\pi^*)_{\text{Flu}} \leftarrow (\pi)_{\text{NPh}_2}$ |
| | 301 [55.1] | 303 [0.32] | 192 (57%) | → | 198 $(\pi^*)_{\text{NPh}_2} \leftarrow (\pi)_{\text{Flu/Ph}}$ |
| | | | 191 (34%) | → | 197 $(\pi^*)_{\text{NPh}_2} \leftarrow (\pi)_{\text{Flu/Ph}}$ |
| | | | | | |
| 6 | 385 [83.2] | 405 [2.04] | 166 (94%) | → | 167 $(\pi^*)_{\text{Flu}} \leftarrow (\pi)_{\text{Flu/NPh}_3}$ |
| | / | 304 [0.25] | 166 (54%) | → | 172 $(\pi^*)_{\text{NPh}_2} \leftarrow (\pi)_{\text{Flu/Ph}}$ |
| | 301 [35.6] | 303 [0.20] | 164 (62%) | → | 167 $(\pi^*)_{\text{Flu}} \leftarrow (\pi)_{\text{Flu/NPh}_3}$ |

[a] The calculated excited states are ${}^1\text{A}$. [b] Experimental absorption (nm) and extinction coefficients (ϵ) in $10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$. [c] in nm. [d] Computed transition moment under vacuum. [e] Experimentally not determined.

11. Experimentally Observed (CH_2Cl_2) vs. Computed (Vacuum) UV-vis Absorption Spectra

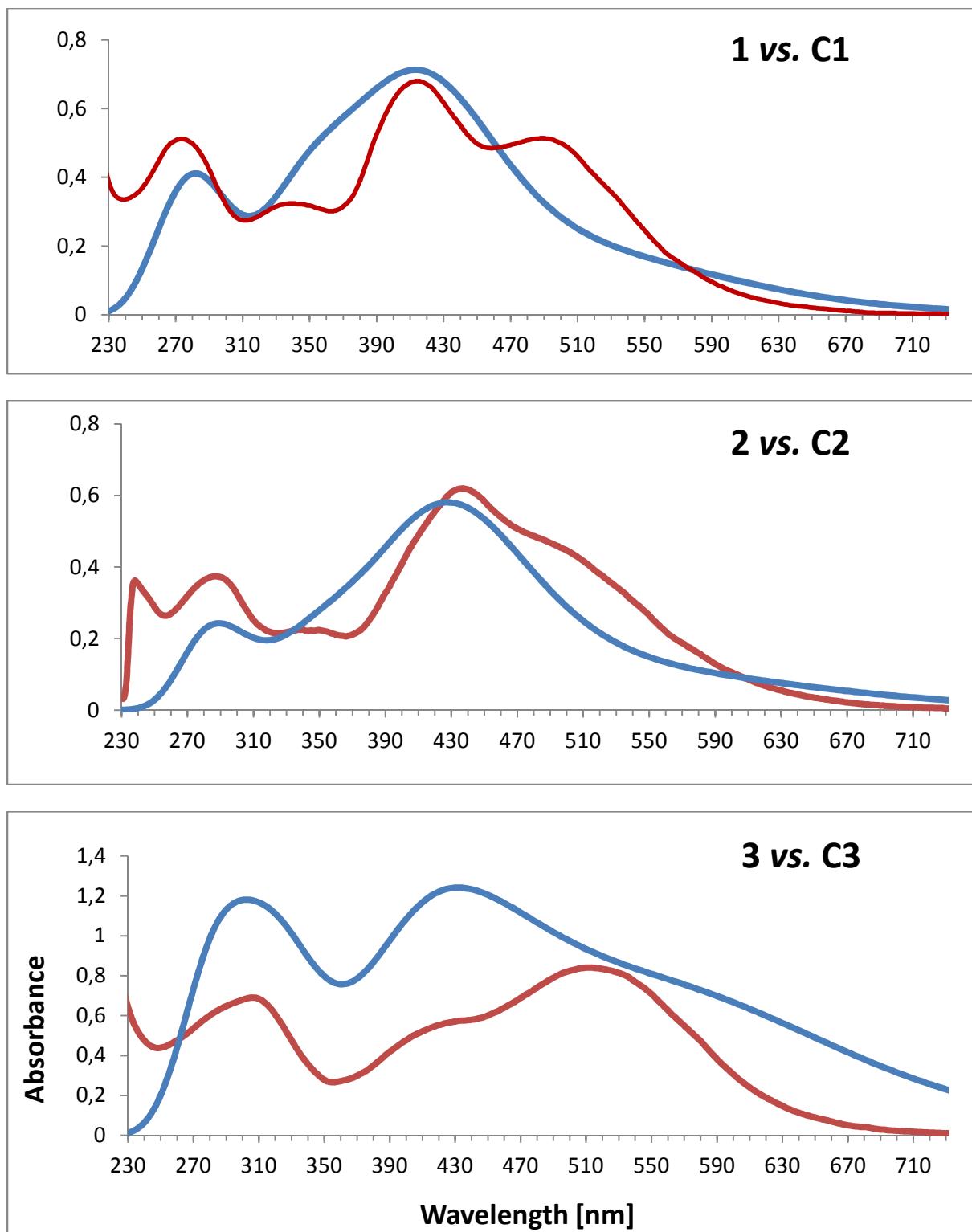


Figure S20. Experimental (red) vs. TD-DFT-computed (blue) spectra for **1-3**. A Gaussian broadening function has been applied to the DFT calculated spectra (half-width: 0.4 eV).

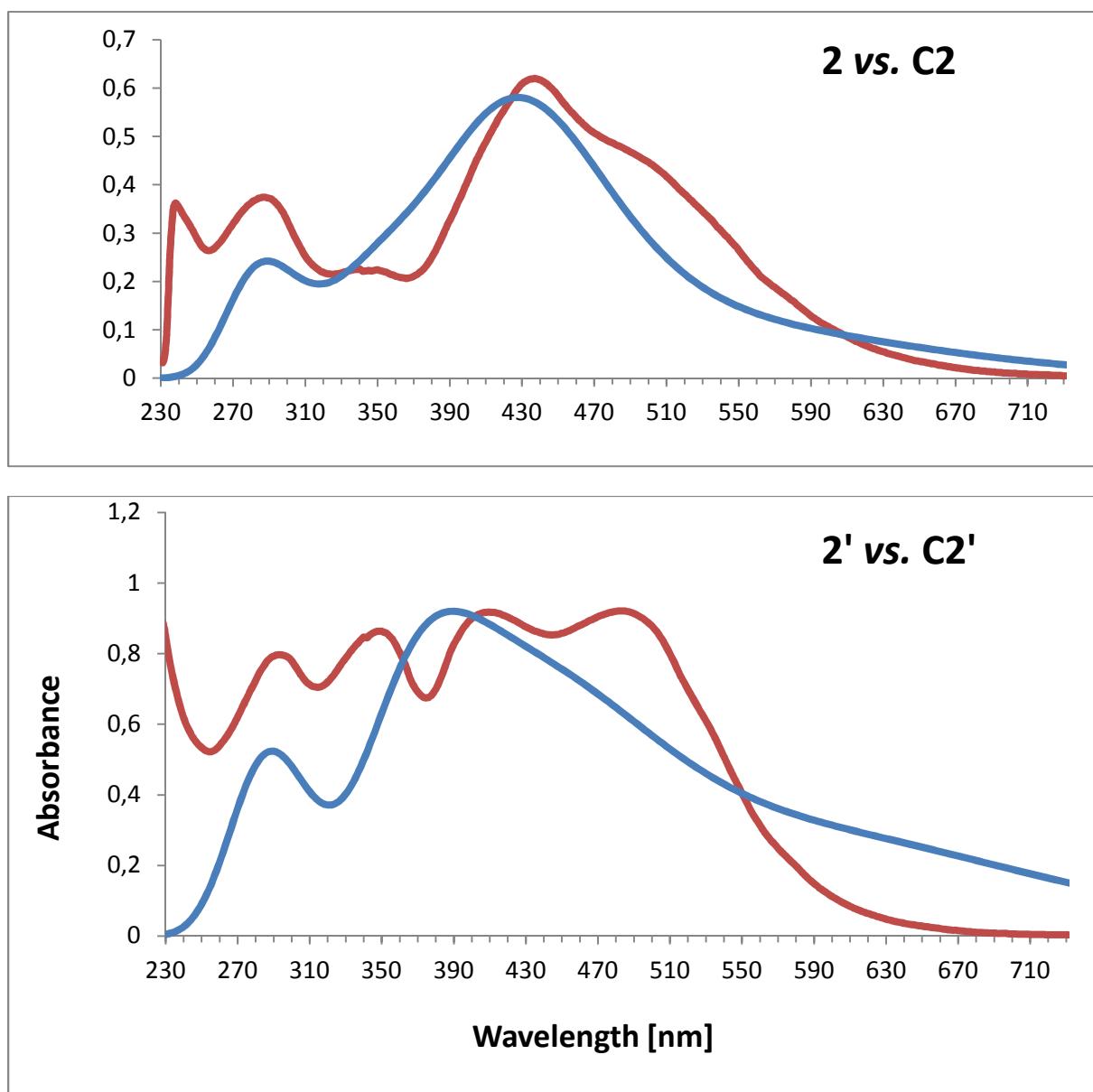


Figure S21. Experimental (red) vs. TD-DFT-computed (blue) spectra for **2** and **2'**. A Gaussian broadening function has been applied to the DFT calculated spectra (half-width: 0.4 eV).

Supporting Information

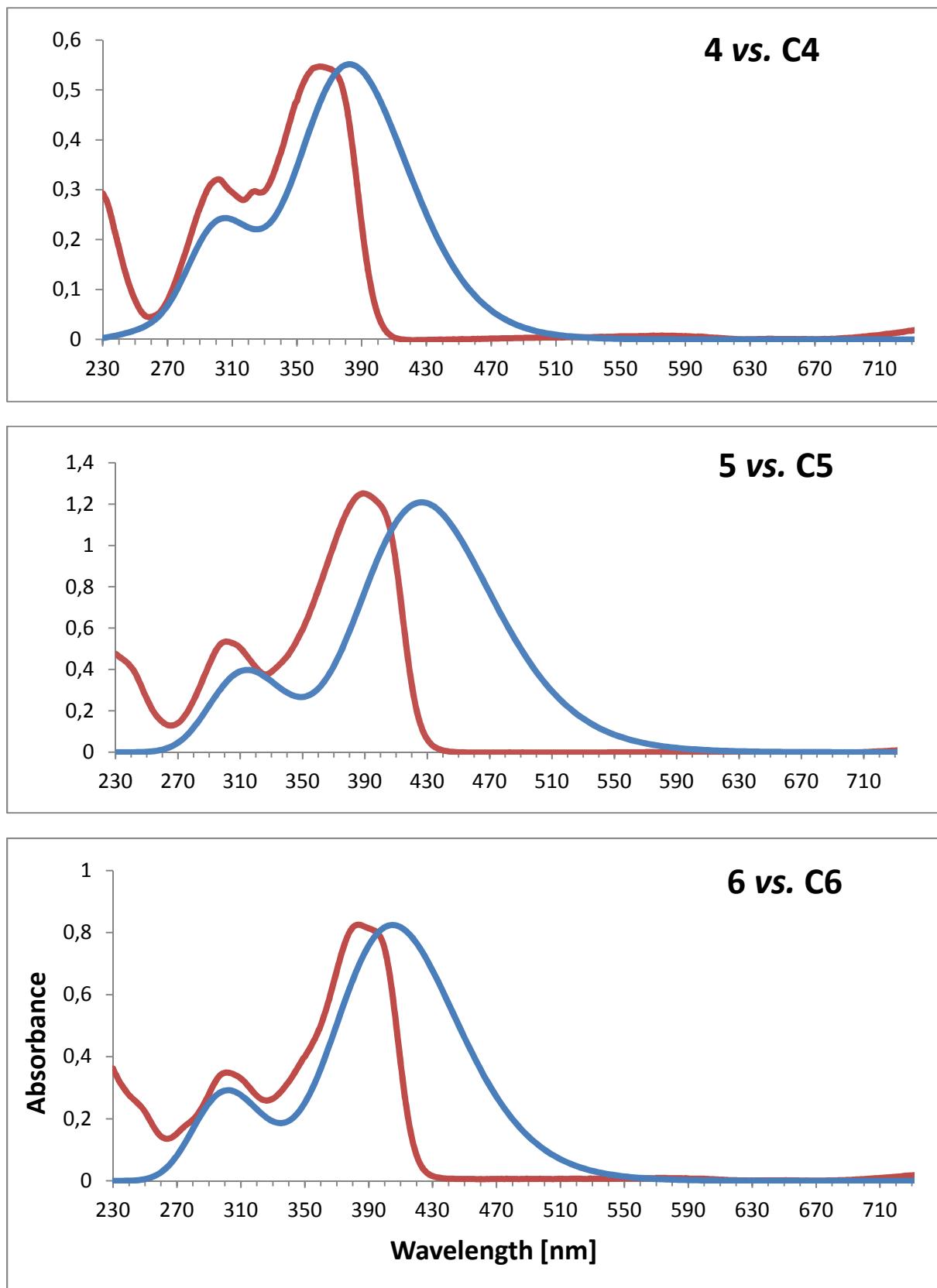


Figure S22. Experimental (red) vs. TD-DFT-computed (blue) spectra for **4-6**. A Gaussian broadening function has been applied to the DFT calculated spectra (half-width: 0.4 eV).

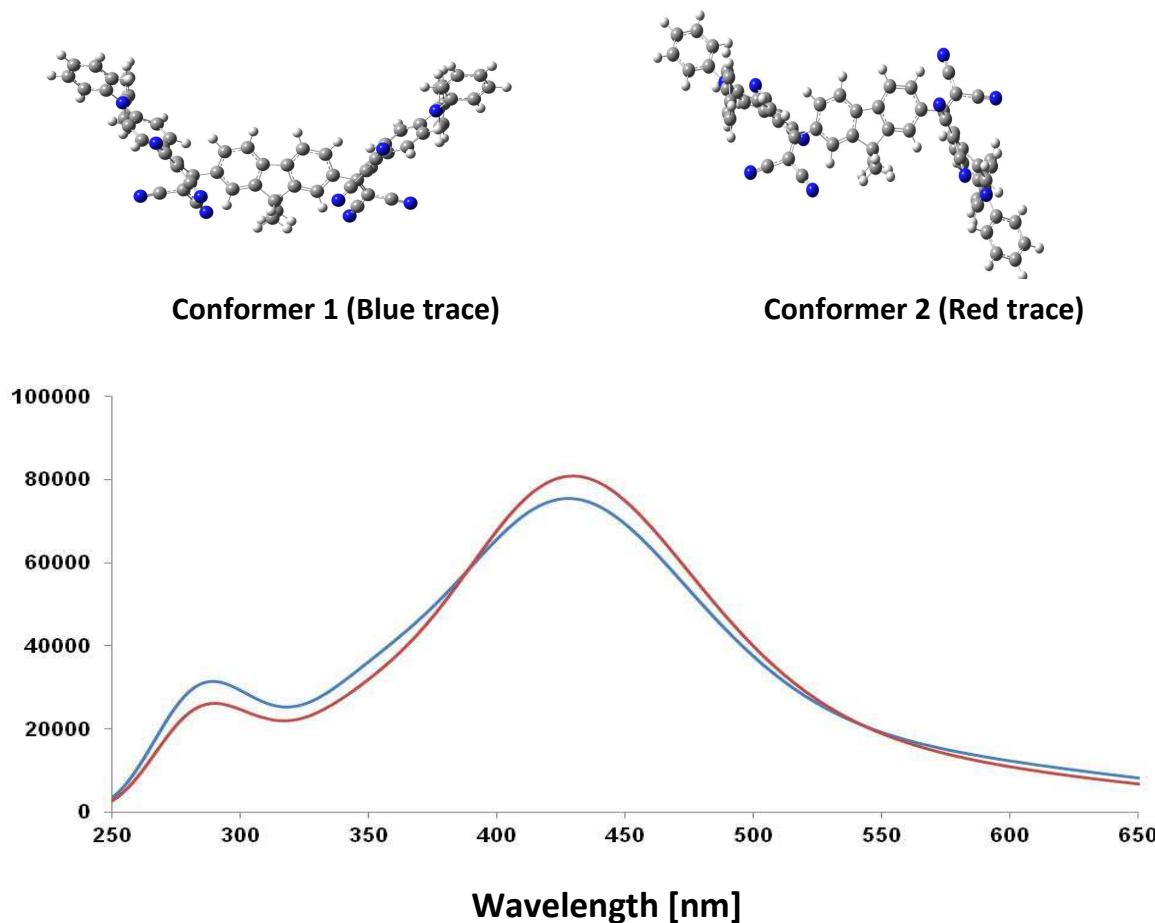


Figure S23. TD-DFT-computed spectra for two conformers of **2**. A Gaussian broadening function has been applied to the DFT calculated spectra (half-width: 0.4 eV).

12. Characteristic Stretching Modes Experimentally Observed (KBr Pellets) and Computed (Vacuum) for **1-6** and **C1-C6**, respectively

Table S5. Calculated (top)^[a] and experimental (bottom) vibrational frequencies (cm^{-1}) of the $\nu_{\text{C}\equiv\text{C}}$ and $\nu_{\text{C}\equiv\text{N}}$ stretching modes in compounds **C1-C6** and **1-6**, respectively.

| Compound | | | | | | |
|----------------------|---------------|---------------------------------|---------------|----------------------|----------------|----------------|
| 1^a | 2 | 2' | 3 | 4^a | 5 | 6 |
| <i>Calc</i> | | | | | | |
| 2240 (m, C≡N) | 2249 (m, C≡N) | 2254 (m, C≡N), 2212 (m, C≡C) | 2256 (m, C≡N) | 2216 (w, C≡C) | 2216 (s, C≡C) | 2215 (vw, C≡C) |
| <i>Exp</i> | | | | | | |
| 2219 (m, C≡N) | 2222 (s, C≡N) | 2221 (m, C≡N) 2195 (vw, C≡C) | 2223 (s, C≡N) | 2197 (vw, C≡C) | 2194 (vw, C≡C) | 2197 (vw, C≡C) |

[a] Scaling factor of 0.951 used.

13. Z-Scan Data for 1-3 and 2'

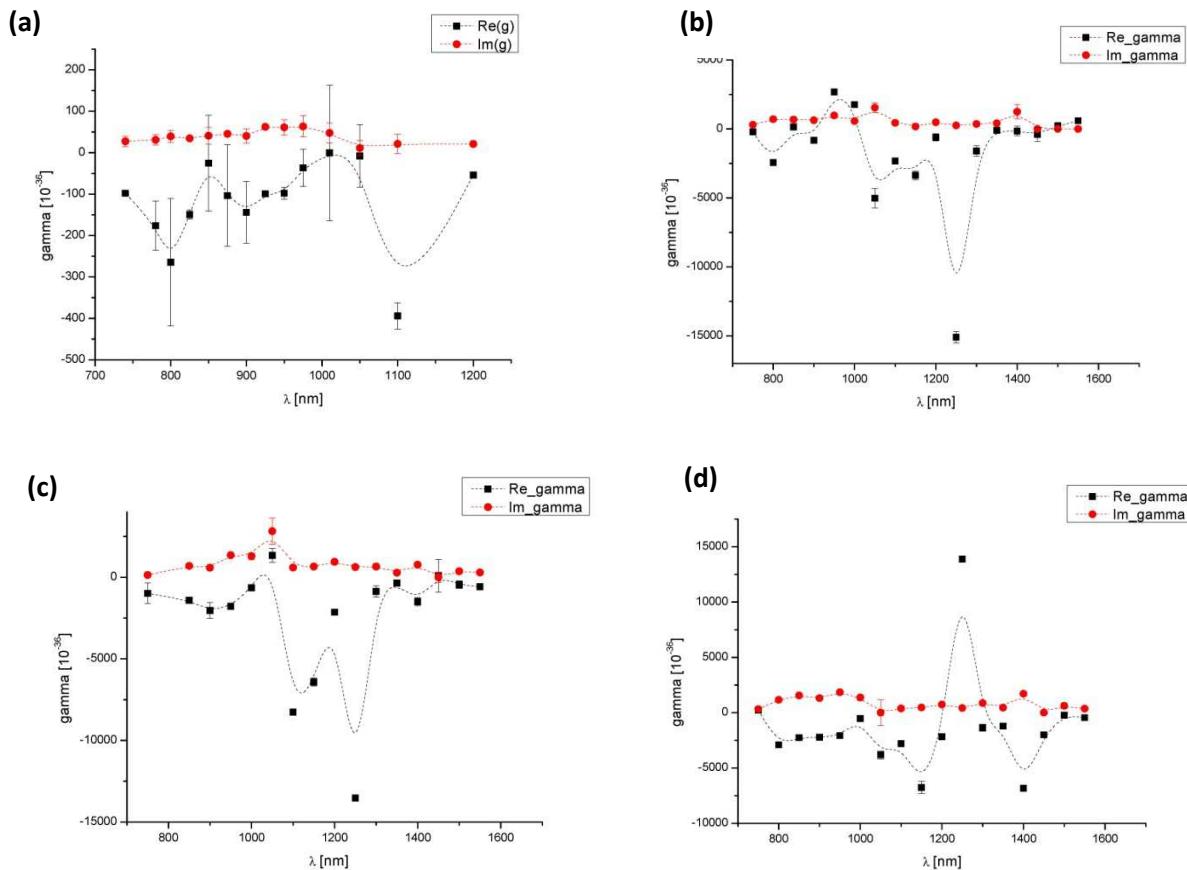


Figure S24. Overlay of real and imaginary cubic nonlinear optical molecular coefficients derived from closed- and open-aperture Z-scan measurements for **1** (a), **2** (b), **3** (c) and **2'** (d) in CH_2Cl_2 (b-d) or THF (a) at 25 °C.

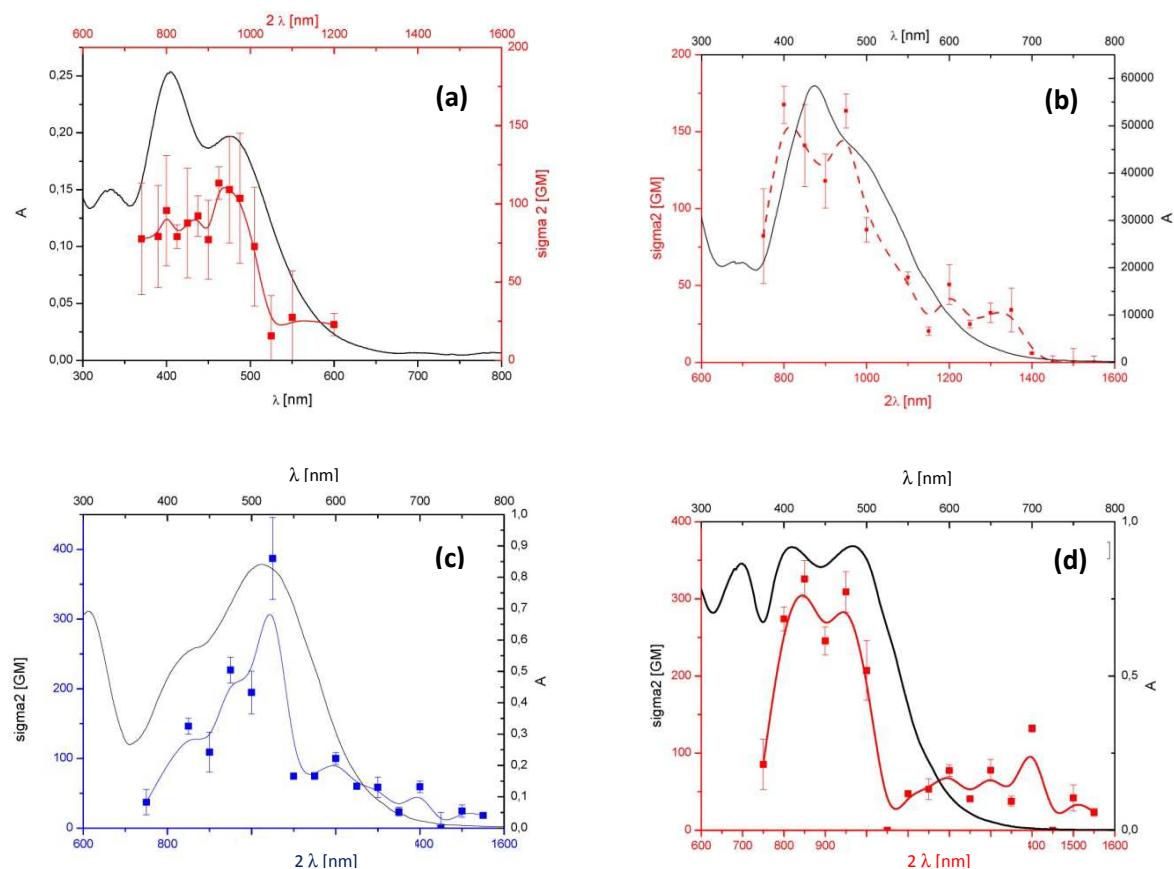


Figure S25. Overlay of one- and two-photon absorption spectra for **1** (a), **2** (b), **3** (c) and **2'** (d) in CH_2Cl_2 (b-d) or THF (a) at 250 °C. The two-photon cross-sections are derived from open-aperture Z-scan measurements and the one-photon spectra are plotted against twice the wavelength (2λ).

14. Two-Photon Excited Fluorescence (TPEF) Data for 4-6

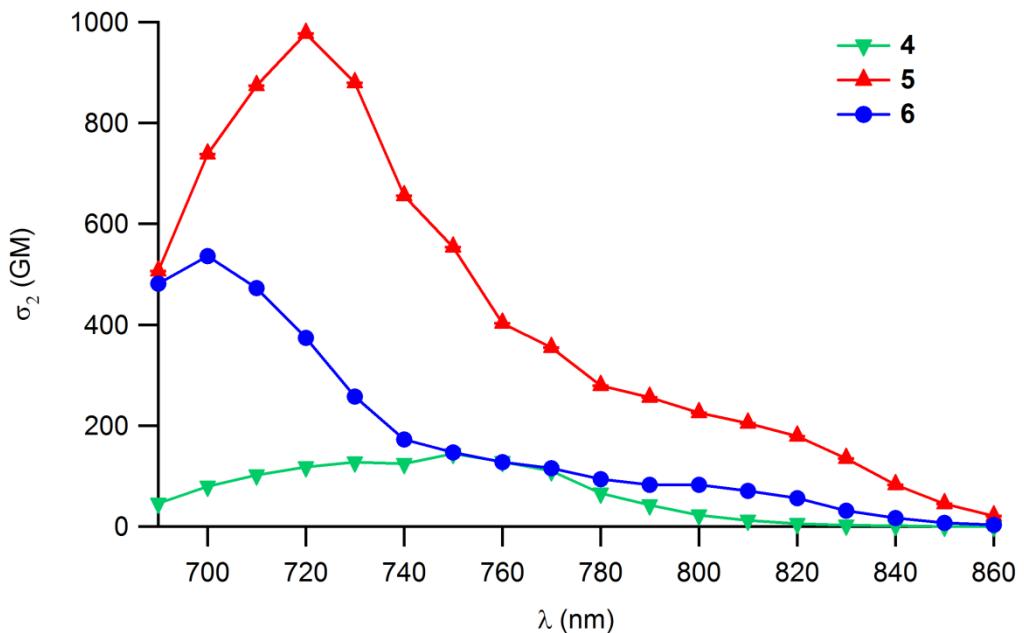
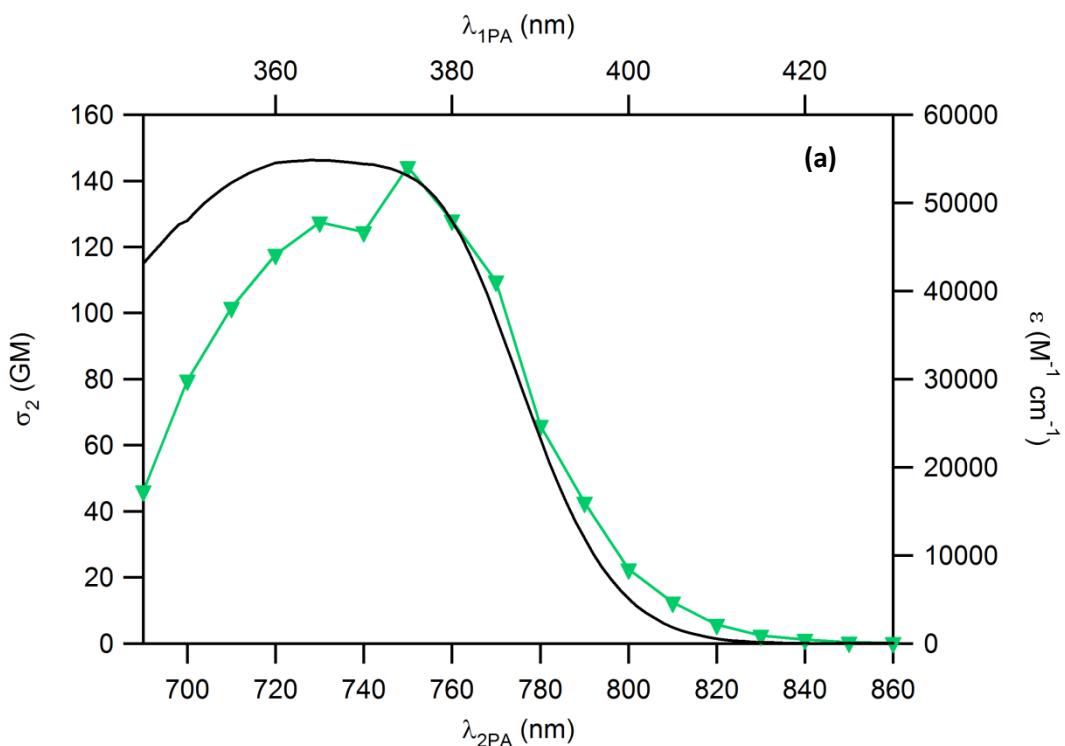


Figure S26. Two-photon absorption spectra of **4-6** in dichloromethane (25 °C) in the Near-IR range.



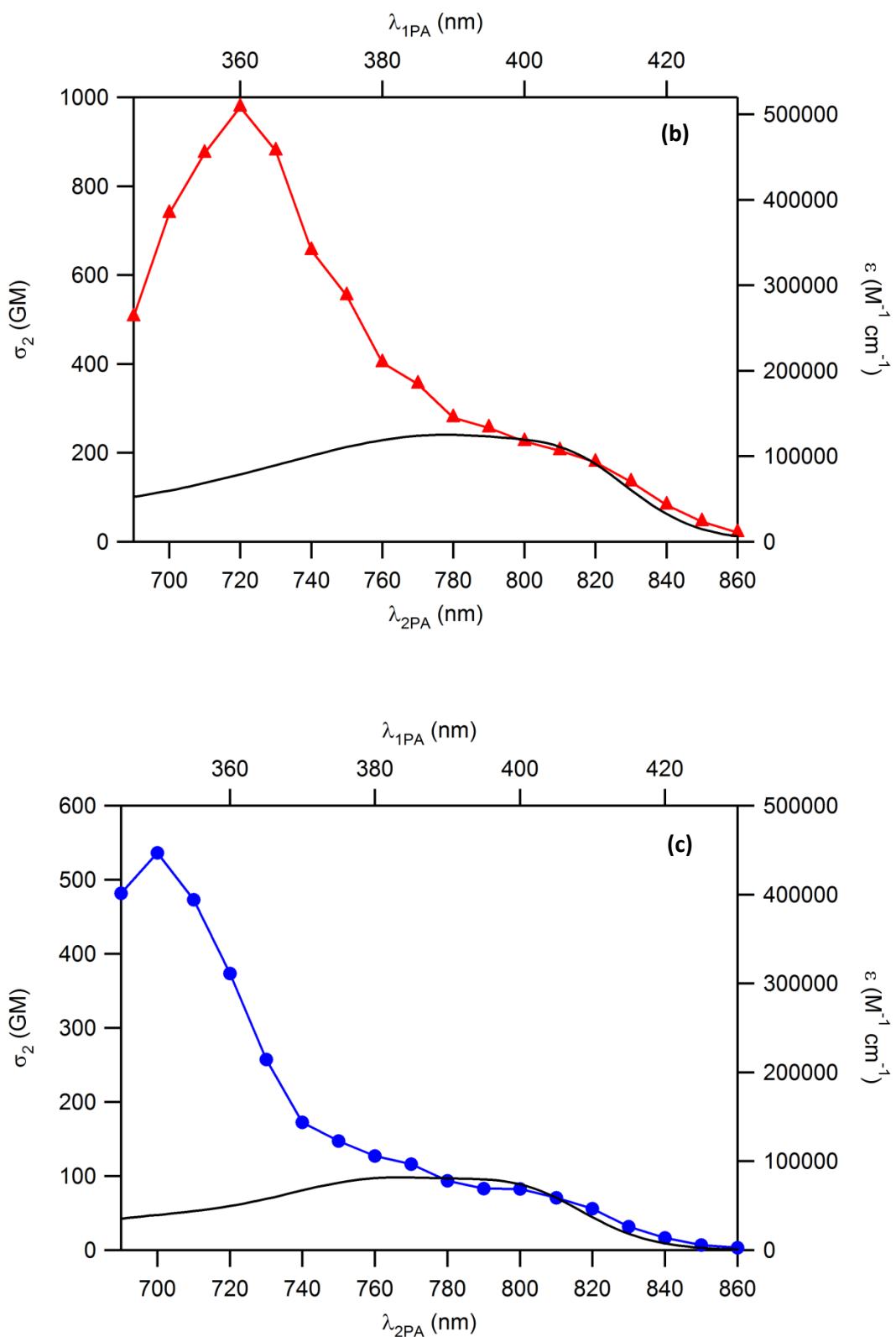


Figure S27. Overlay of one and two-photon absorption spectra for **4** (a), **5** (b) and **6** (c) in CH_2Cl_2 (25°C).